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Forestry impact on upland water quality

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Abstract

The results of extensive monitoring of major, minor and trace element variations in rainfall, throughfall, stemflow and stream water in a Sitka spruce plantation at Plynlimon, mid-Wales, are presented. The study describes the hydrogeochemistry of a UK upland site while providing detailed assessment of the environmental impacts of conifer harvesting and acidic oxide deposition.

Rainfall inputs are chemically variable, influenced by maritime, pollutant and land-derived inputs. Stemflow and throughfall chemistry show a similar behaviour to the rainfall, but their higher concentrations are due to enhanced mist capture and dry deposition onto the vegetation surface. Stream water chemistry is determined primarily by hydrological flow pathways and by chemical reactions in the surface organic soils and in the underlying inorganic soils/bedrock. Chemical reactions in the organic horizons generate acidic conditions and mobilise transition metals. Decomposition processes in the soil are important in determining the hydrochemical behaviour of the nutrients. In the inorganic zones, reactions involve hydrogen ion consumption and base cation release. There is a net output of many inorganic components from the forested catchments: this is the result of weathering reactions and chemical supplies from the bedrock. The nutrients which are supplied from the atmosphere are retained within the catchment. Hydrograph separation techniques show that the chemical response to rainfall events can be explained broadly in terms of increased contributions from the upper soils at high flow: groundwater contributions are significant at all flow levels. However, detailed analysis reveals that stream water is composed of a mixture of water from many chemically distinct sources.

Tree harvesting at Plynlimon results in a deterioration in stream water quality for those components that are known to affect stream ecology (hydrogen ion and aluminium). Harvesting reduces shading of the stream, causing higher temperatures during the summer months: this results in the presence in the stream of a higher proportion of the environmentally-harmful forms of aluminium. While increased nitrate production is observed, this will probably not be of environmental concern: the concentrations remain relatively low while the system remains phosphate-limiting for enhanced algal generation. Potential water treatment problems associated with colour and water chlorination are highlighted.

Contents

1 Introduction

Considerable evidence has been accumulated which shows that acidification of the UK upland environment has occurred. The first phase of soil acidification probably started up to ten thousand years ago with the development and subsequent loss of birch, hazel, alder and oak forests (Dimbleby, 1952; Taylor, 1974; Pennington, 1984). The deforestation occurred during Neolithic and Bronze Age times because of a deteriorating micro-climate (about 2700 years ago) and local deforestation by man (5000-3000 years ago and in some cases up to the present day). Consequently, thin acidic moorland soils developed and these are characteristic of much of the uplands today. In waterlogged areas, where reducing conditions ensured limited breakdown of organic matter and provided very acidic conditions, peat deposits accumulated. Set against this long-term change in the upland environment, further acidification has occurred during the past hundred years and this has had an adverse effect on upland ecology.

Major concern has been raised about the deterioration in stream water quality in the British uplands, as associated with this second and ecologically potent phase of acidification. Acidic oxide deposition and conifer planting have been implicated as the major factors in this decline (Stoner & Gee, 1985; UKAWRG, 1988; Whitehead *et. al.*, 1988, Jenkins *et. al.*, 1990). Both may lead to the generation of more acidic and aluminium bearing stream water and conditions unhealthy for stream biota. However, it is widely believed that, for the UK, the driving force is the former: conifers enhance the capture of acid pollutants, thereby increasing their impacts; acidification has occurred even for the most extensive tracts of the uplands which had no tree cover. Nonetheless, the relative importance and the degree of interaction of the two factors still needs clarifying (Hornung, 1985; Miller, 1985; Jenkins *et al.*, 1990; Rosenqvist, 1990; Nisbet, 1990; Krug, 1991). For example, under pristine conditions there is evidence both for and against the deleterious effects on stream water of conifer development.

In a modelling study of afforestation, Jenkins *et al.* (1991) comment, "Afforestation in the absence of acidic deposition, however, has had a lesser effect on surface water acidification even though the nutrient demands of forest growth have caused significant soil acidification". While acidification of the soils occurs by 'natural processes', it is the added constraint of changing atmospheric inputs and/or land disturbance that can lead to major changes in the stream. Much of these upland plantations are reaching the harvesting and replanting phases and hence such programmes will accelerate over the next decade (Adamson & Hornung, 1990). These practices could themselves lead to further deterioration of water quality.

Long-term (decadal) modelling predictions suggest that following conifer harvesting in acidic and acid-sensitive areas, water quality will improve, provided that replanting does not occur. Although the models have not been widely applied to studies of replanting, initial work suggests a second and more serious phase of acidification (Jenkins, *et al., 1990).* Such a deterioration will result from continued acidic oxide deposition, coupled with base cation uptake into the biomass: this will reduce an already depleted base cation store in the soil. Field studies suggest that, for a few years after felling, conditions in the soil and stream waters will deteriorate (Likens *et al.*, 1970; Lawrence *et al.*, 1987; Lawrence, 1989; Stevens & Hornung, 1987; Hornung *et al.*, 1989; Adamson & Hornung, 1990) because of factors such as:

- changing hydrological flow pathways altering the proportions of acidic and aluminium-bearing soil waters and less acidic and aluminium-depleted groundwaters entering the stream;

- reduced nutrient uptake by the trees promoting nitrate release to the soil solution, thereby acting as a mobile anion, releasing environmentally-harmful inorganic aluminium and possibly increasing the acidity.

Few publications summarise the effects of conifer harvesting on stream water quality in the British uplands (Hornung *et al.*, 1989; Adamson & Hornung, 1990) although several UK studies are now nearing completion. A brief summary of the conclusions from these is provided in Appendix 1, courtesy of comments made by Brian Reynolds and Paul Stevens of the Institute of Terrestrial Ecology (Bangor, North Wales) and Ron Harriman of the Freshwater Fisheries Laboratory (Pitlochry, Scotland). The locations of these studies are identified in Figure 1. Consequently, there remains a need to identify the spectrum of representative catchment responses to obtain a general perspective. The heterogeneous nature of catchments makes it difficult to assess the impact of conifer harvesting on stream water quality (Neal *et al.*, 1988, 1990a)

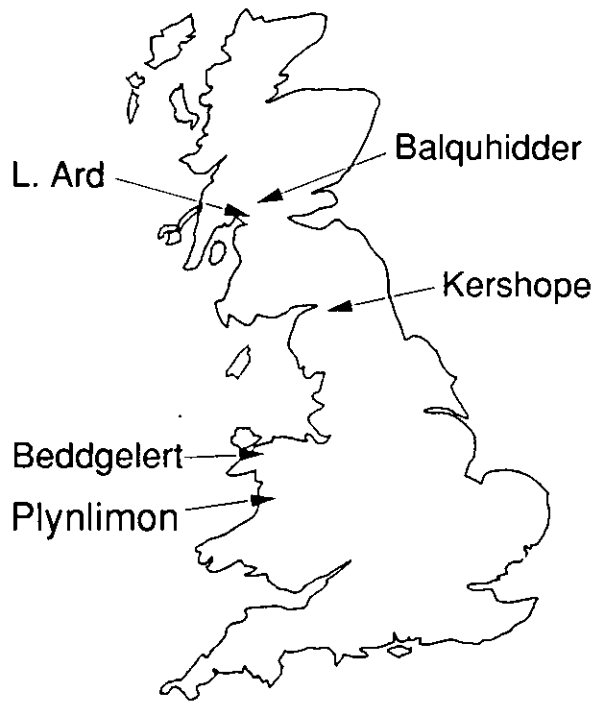


Figure 1 *Location map of UK catchment deforestation studies*

since catchments next to each other, of similar soil type and geology, exhibit different hydrochemical relationships (Reynolds *et al.*, 1986).

In 1983, the project reported on here was instigated to develop an understanding of the importance of land use change in the British uplands by studying water quality changes in forest streams before, during, and after a deforestation programme. Two main subcatchments of the headwaters of the River Severn in the Hafren forest were selected for study. They were chosen because (1) a deforestation programme was planned for one of the two subcatchments, (2) detailed hydrological data for the catchments were available: they form an integral part of the Institute of Hydrology's water balance studies (Newson, 1976; Kirby *et al.*, 1991: see Appendix 2) and (3) complementary chemical studies within the area were being undertaken by staff of the Institute of Terrestrial Ecology (Bangor).

The overall project objective was, and remains, to continue and develop further studies on the movement through forested catchments of key elements which directly affect water quality or are relevant to the understanding of processes which affect water quality. Within this context, there are three themes:

1 to understand, at the catchment scale, variations in water quality with hydrology and land use change;

2 to assess changes in stream water chemistry, for a wide spectrum of elements, prior to, during and subsequent to deforestation for one catchment in the Upper River Severn;

3 to develop hydrochemical models of the Plynlimon catchments for process and management applications.

This report gives a general overview of the work so far.

2 The Plynlimon Study

2.1 Study area

The work relates to two streams, the Afon Hafren and the Afon Hore, which form the main headwater drainage of the River Severn in mid-Wales (Figure 2).

Bedrock geology consists of lower Palaeozoic mudstones, greywackes, sandstones and grits. This is covered by a thin soil, typically 70 cm thick, with organic-rich 'L' and 'O' horizons (3 to 10 cm). The lower soils consist of a leached 'E' horizon (10 to 20 cm) and a fine-textured podzolic 'B' horizon (about 40 cm thick) merging into a stone 'C' horizon. The predominant soil is a stagnopodzol, but peat, brown earth and stagno-gley soils also occur within the two subcatchments (Figure 3). At the top of each subcatchment, acid grassland is dominant — vegetated mainly with *Nardus* and *Agrostis*

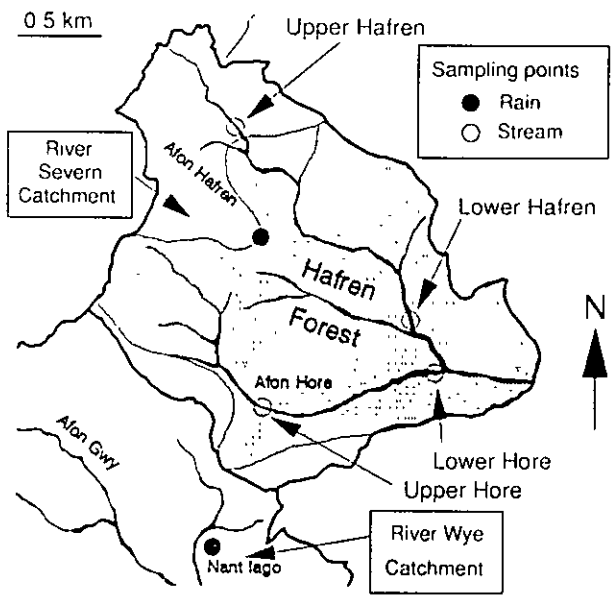


Figure 2 *The Plynlimon study area*

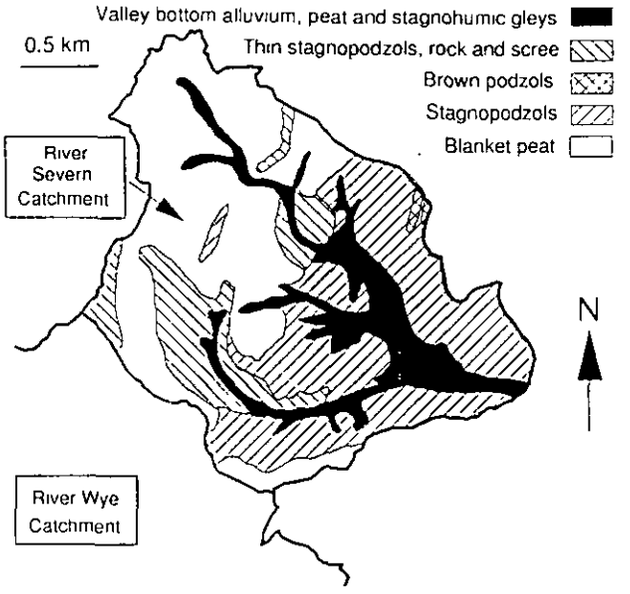


Figure 3 *The soils of Plynlimon*

species. *Eriophorum* species predominate on peat areas. On the lower parts of the two sub-catchments, plantation forestry (predominantly Sitka spruce, *Picea sitchensis*) was introduced in various phases between 1937 and 1964, onto acid moorland. The areal coverage of the forest before harvesting amounted to 50 per cent of the Afon Hafren and 77 per cent of the Afon Hore.

Apart from minor 'thinning' of the forest stand, harvesting did not begin until late spring 1985 when clear felling of the lower half of the Afon Hore commenced. This felling took four years to complete (Figure 4). Several types of tree removal process were employed (skidding, forwarding and skylining): whole tree harvesting was not used. In the process, extensive brash and tree stumps were left to decompose *in situ*. Soon after harvesting, the slopes were replanted with juvenile Sitka spruce (<1m high). Rainfall averages about 2500 mm y^{-1}, with evapotranspirational losses typically amounting to 500 and 650 mm y^{-1} for the Afon Hafren and Afon Hore respectively. Being next to each other, of similar altitude range (360–470 m) and similar size (about 340 ha), the streamflow responses to storm events are similar and in phase for the two sub-catchments: the hydrograph response to storms is both rapid and 'flashy'; flows vary between 0.01 and 4.5 m^3s^{-1} (Newson, 1976; Kirby *et al.*, 1991). Full details of the hydrological and sedimentological findings for the Plynlimon study area are given in Appendices 2 and 3.

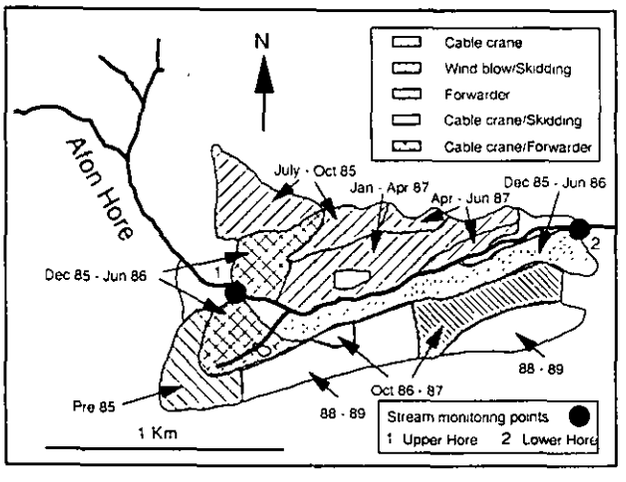


Figure 4 *Forest felling record*

2.2 Sampling programme

Weekly sampling for detailed chemical analysis of rainfall and Afon Hafren and Afon Hore stream water has continued since May 1983. Stream water was collected by "grab sampling" while rainfall was represented by a bulked sample taken from two gauges spanning the altitude range for the catchments. Initially, the Afon Hafren stream was monitored to provide a control in juxtaposition to the deforestation programme for the Afon Hore.

Unexpectedly, it was found that small differences in the degree of calcium carbonate mineralisation in the bedrock lead to important hydrochemical differences between the two streams. In particular, the Afon Hore has higher pH (typically by 0.5 pH units) and higher base cation concentrations (by a factor of about 4). Thus, the Afon Hafren proved to be inappropriate as a control. Therefore, the Afon Hore was sampled at a second point, above the harvest area, to act as a substitute control (Figure 2). This upper Hore site is about half-way between the top of the catchment and the lower Afon Hore monitoring point. Monitoring began in September 1984.

Further extensions to the monitoring scheme have also been introduced:

1 stemflow and throughfall samples were collected to allow a more complete assessment of atmospheric inputs to the catchment (from February, 1984);

2 Afon Hafren stream water was collected upstream of the forest area to obtain hydrochemical data for future comparison with the lower Afon Hafren stream chemistry when felling occurred and to provide new information on an acid moorland stream (from May 1990);

3 a tributary of the Afon Hore was sampled (south2-Hore). This provided information, from April, 1988, on the chemical variations

occurring before, during and post felling, for an area draining forest soils with minimum groundwater inputs;

4 to allow assessment of occult deposition (from February 1989), fine mist was collected near the top of the Severn catchment using a system designed by the Institute of Terrestrial Ecology (Edinburgh);

5 continuous pH and conductivity monitors were installed near to the Institute of Hydrology's Staylittle office to monitor rainfall, stemflow and throughfall (from August, 1988);

6 continuous pH and conductivity monitors were introduced at the upper and lower stretches of both the Afon Hafren and Afon Hore during 1989 to allow assessment of short-term chemical variations.

2.3 Chemical analysis

Water samples were filtered either immediately on collection in the field (stream waters) or immediately on return to the laboratory (rain, throughfall, stemflow and cloud water). Filtered samples were stored and analysed as follows. 0.45 μm membrane-filtered samples were stored (at 4°C in the dark) in HCl-washed (10% v/v) polypropylene bottles with 'Aristar' HNO_3 (1% v/v). All the samples, except the cloud waters, were pre-concentrated twenty-fold by evaporation and analysed using inductively coupled optical emission spectroscopy and plasma emission mass spectrometry for major, minor and trace metals. 2 μm glass fibre filtered samples, stored in chromic-acid-washed glass bottles (also in the dark at 4°C), were analysed using automated colorimetric techniques for F, Cl, Br, I, NO_3, PO_4, NH_4, and Si. Dissolved organic carbon was determined using a TOCsin II aqueous carbon analyser.

The detection limits varied for the different determinands. In some cases, the range of concentrations measured reached down to the detection limits. In other cases, the concentrations were well above the detection limits and such resolution was not required. For the major components, the lowest quoted values (in mg l^{-1}) are about 0.1 for Na, Ca and Mg, 0.04 for K and SO_4, 0.1 for Si and NO_3 and 0.2 for DOC and Cl. For the trace constituents, the lowest quoted values (in μg l^{-1}) are about 0.1 for Sr, Ba, Co, Mn, Y and I, 0.4 for Li, 1.5, for B, Cu, Fe, Zn and Br and 0.05 for the other components as determined by plasma emission mass spectrometry.

Electrometric techniques were used to determine pH, alkalinity and acidity, by titration, on unfiltered samples. For the titrations, reagents, electrodes and water samples were maintained at field temperature to minimise interferences: CO_2 degassing was minimised by storing the samples in fully sealed glass bottles. During the acidity titration, reactants and titrants were kept in a nitrogen atmosphere to eliminate atmospheric CO_2 contamination.

For the continuous pH and conductivity measurements, pHOX systems were used in conjunction with gel-filled combination electrodes specifically designed for low conductivity waters. Considerable time and effort went into maintaining the monitoring equipment to a satisfactory analytical standard: each week the electrodes were thoroughly cleaned and the system was re-calibrated using standard pH 4 and 7 buffers that were kept at the same temperature as the stream. To check the quality of the readings, additional measurements were taken about the time of weekly calibration. To do this, the pH registered by the continuous monitor was taken immediately before and immediately after calibration — these values were compared with a laboratory measurement of a water sample collected at the same time.

3 Hydrochemical behaviour of the Hafren Forest

3.1 Atmospheric inputs

Plynlimon rainfall is derived from a variety of sources and therefore has a chemical composition that is highly variable (Table 1). Being close to the Irish sea and the North Atlantic Ocean, westerly winds provide rainfall enriched with sea spray. In contrast, winds from other directions bring air that has passed over agricultural land and industrial areas: this provides rainfall low in sea salt but enriched with lithogenic (e.g. silica) and pollutant (heavy metals, sulphate, nitrate and ammonia) components. Because of the varying meteorological conditions, five types of behaviour are observed for the chemical constituents in rainfall:

Table 1a *Flow weighted means and ranges for rainfall, throughfall, stemflow and cloud-water. All concentrations are in $\mu g l^{-1}$ with the exception of pH (dimensionless), acidity and alkalinity ($\mu Eq l^{-1}$). The mean pH values were calculated from the flow weighted mean hydrogen ion concentration.*

	Rainfall	Through-fall	Stemflow	Cloud-water
Na	2 6 (0-24)	15.2 (2-94)	16 2 (2-66)	123 0 (3-419)
K	0.13 (0-0 9)	4.50 (1-26)	6.20 (1-50)	4.62 (0.2-16)
Ca	0.18 (0-2)	1.92 (0-18)	2.5 (0-22)	5.1 (1-15)
Mg	0.3 (0-3)	2 8 (0-20)	2.8 (0-24)	15 0 (0-51)
SO_4	1.6 (0-9)	14.6 (3-178)	20.5 (3-201)	37 8 (8-106)
Si	0.34 (0-20)	0.15 (0-0.5)	0.16 (0-1.3)	0.03 (0-0.3)
DOC	0.4 (0-3)	6.7 (1-56)	13.2 (2-128)	1.6 (0-12)
NO_3	0 8 (0-75)	2.9 (0-45)	3.7 (0-72)	10.8 (2-69)
NH_4	0.3 (0-5)	0.9 (0-9)	0.1 (0-14)	3 3 (1-24)
PO_4	0.04 (0-2)	0 14 (0-2)	0.14 (0-2)	0.03 (0-0.2)
F	0.03 (0-0.23)	0.08 (0-0.33)	0.09 (0-0.54)	0.06 (0-0 41)
Cl	5.1 (0-44)	31.9 (4-194)	33.5 (3-144)	220.0 (2-740)
pH	4.79 (3.4-7.7)	4.50 (3.6-6.1)	3 91 (3.2-4.6)	4.28 (3.5-6.0)
Acid	64.7 (-446-630)	365.6 (37-1207)	499.0 (-112-2508)	306.0 (20-1968)
Alk	-6 7 (-437-201)	-30.0 (-251-79)	-123.0 (-708-117)	-48.1 (-398-31)

Table 1b *Flow weighted means and ranges for trace element constituents in rainfall, throughfall, stemflow and cloud-water. All concentrations are in $mg l^{-1}$ with the exception of conductivity ($\mu S\ cm^{-1}$). Y, Co, Cd, Sc, V, La, Zr and Mo data are not included as their concentrations were usually below the detection limits; the few remaining values were outlier points.*

	Rainfall	Through-fall	Stemflow	Cloud-water
B	3.4 (0-44)	32.2 (9-121)	33.1 (9-112)	15.0 (0-100)
Li	0 1 (0-0 7)	0.6 (0-2 3)	0 7 (0-4.4)	4.3 (0-11)
Sr	2.1 (0-14)	12.1 (2-82)	14 4 (1-127)	83.1 (4-274)
Ba	1.6 (0-67)	5.3 (0-30)	8 7 (0-58)	5 0 (0-28)
Mn	1 2 (0-27)	676 9 (104-9162)	1232.0 (90-10902)	9.5 (0-62)
Cu	1.6 (0-35)	N/A	14.1 (0-2528)	2.5 (0-28)
Fe	6.6 (0-98)	24.3 (8-183)	51.7 (5-262)	27.5 (0-256)
Zn	9 2 (0-186)	N/A	9.5 (6-1090)	63.1 (0-400)
Al	8 0 (0-137)	59.1 (12-586)	79.1 (9-759)	63.8 (10-350)
Be	<0.01	<0.01	0 018 (0-0.17)	0.29 (0-0 5)
Ni	0.4 (0-16)	13.9 (2-157)	22 8 (0-212)	1.7 (0-20)
Pb	6.0 (0-131)	3 7 (0-71)	2 8 (0-25)	13 7 (0-120)
Cr	2.3 (0-34)	5 4 (1-42)	4.5 (0-32)	3.4 (0-12)
Br	18.7 (3-128)	123.2 (22-600)	140.5 (24-475)	685.5 (9-2300)
I	1 3 (0.6-10 5)	4.3 (1.2-33.3)	6.1 (1.4-42)	11.3 (0.8-17.0)
Cond.	27 4 (7-190)	160.4 (30-620)	220 0 (39-030)	754 0 (1-324)

1 Sodium, magnesium, strontium, bromide and chloride are components of rainfall which come from marine sources. They are transferred from the sea to the atmosphere as sea-spray. Although the rainfall concentrations of these components are highly variable, the ratios of their concentrations remain close to those of sea-water (Figure 5).

2 Iodine in rainfall is also derived from sea spray. However, in the process of transfer from the sea to the atmosphere, it is erratically fractionated at the air-sea interface. Consequently, the ratios of iodine to the other sea salt components are 100 times higher than those for sea water, and iodine concentrations are poorly correlated with the other sea salt components ($r<0.2$, $n=274$).

3 Concentrations of the non-sea-salt components in rainfall are highly variable and have low correlations due to their diverse sources: only DOC, ammonia, aluminium and iron are correlated ($r>0.7$, $n=274$).

4 A composite pattern is observed for components that have both maritime and industrial

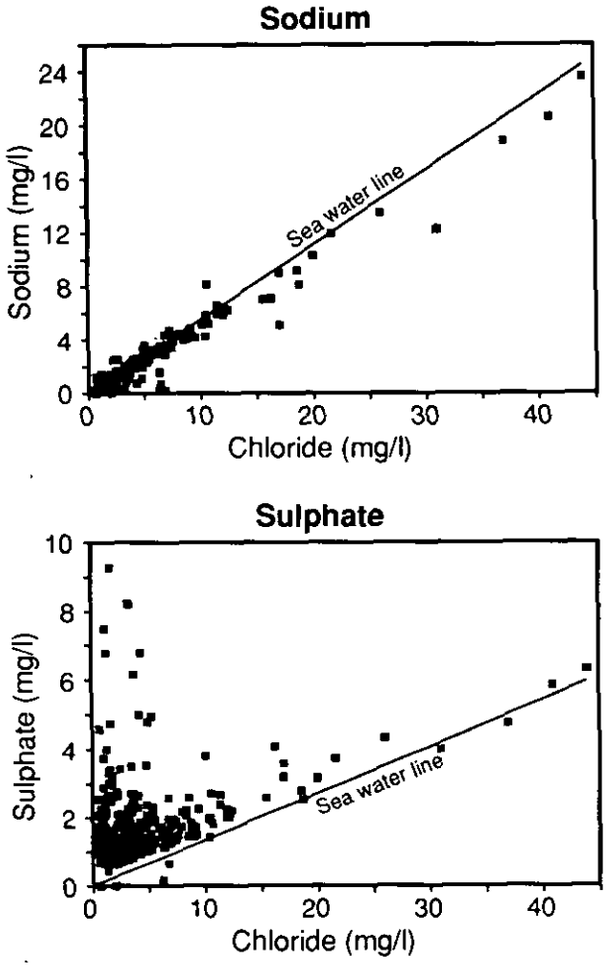


Figure 5 *Sodium and sulphate concentration relationships with chloride in rainfall*

sources (e.g. calcium, sulphate and potassium): concentrations are at their lowest at intermediate sea salt levels (Figure 5).

5 Rainfall concentrations are not correlated at statistically significant levels with volume of catch (many other studies report an inverse correlation which is due to particle washout processes in the atmosphere: this process does not seem to be important at Plynlimon).

Even under conditions where the maritime influence is at its greatest, pollutant inputs of acidic oxides and the transition metals are observed. This feature is particularly pronounced for sulphate as shown by a plot of sulphate versus chloride concentration: at high chloride values, the data follow a line parallel to, but offset from, the marine gradient (Figure 5). Although the marine input is negligible, there is a low but measurable heavy metal content, particularly at high sea salt concentrations.

The trace metal concentrations in rainfall at Plynlimon are low compared with many areas of the UK due to the lack of heavy industry in the region. For nitrogen, sulphur and ammonium, concentrations are moderate for the UK and are associated with long range transport of industrial and farming emissions. Despite these low concentrations, the high annual rainfall means that the total pollutant load entering the catchment is relatively high.

Stemflow and throughfall chemistry resembles that of the rainfall patterns. For example, the concentrations of the sea salt components, sodium, chloride and bromide, are highly correlated ($r > 0.9$, $n = 138$) while many pollutant constituents are maximal at low sea salt levels. However, there is also evidence of biological regulation. For throughfall, Mg, Ca, SO_4, Sr, Ni, Cd, Mn, V and DOC are intercorrelated ($r > 0.7$, $n = 137$). For stemflow, two groupings occur: Ca, Mg, Si, Mn, K, Co, Zn, Ba, Al, Be, Ni, Cd, Pb, NO_3, alkalinity, and hydrogen ion; DOC, B, Fe, NO_3, NH_4, PO_4 and I. The effect of biological cycling is particularly pronounced for constituents such as manganese and dissolved organic carbon with highly enhanced levels in stemflow and throughfall. Concentrations of most elements occur in the order stemflow > throughfall > rainfall (Table 1). This reflects both the cycling effect of the vegetation and the ability of trees to enhance element deposition by capture of fine mist and dry particles from the atmosphere.

In mist, concentrations of sea salt and acidic oxide components are high but they are low for the heavy metals (Table 1). The maritime influence is shown by high inter-correlations for Na, K, Ca, Mg, B, Sr and SO_4. Most of the non sea salt components are not correlated, reflecting a diversity of sources: there are two groups with correlation coefficients greater than 0.7 ($n=23$); Ba, Mn, Cu, Fe, DOC, NO_3, NH_4 and F; Y, Li, Ni and Sc. As with rainfall concentration, pollutant inputs are at their highest when the sea salt components are at their lowest.

The much higher levels of sea salt in throughfall and stemflow, compared to rainfall, illustrate the importance of enhanced capture of mist and dry deposition near forest edges. Sampling points were within 50 metres of the edge of the forest; previous results show lower concentrations of some elements for sampling sites in the centre of the forest. While the results indicate the potential for the trees enhancing atmospheric deposition of chemicals, the extent of the capture cannot be gauged owing to the difficulty of separating the different components making up throughfall chemistry.

With regards to the pollutant loadings entering the Plynlimon catchments, the total levels cannot be accurately gauged owing to uncertainties in the amount of dry and mist deposition. In terms

Table 2 *Wet deposited non-marine sulphate, nitrate and ammonium in Plynlimon rainfall: a comparison with UKRGAR (1991) data for the United Kingdom. The Plynlimon data cover the period from May 1983 to May 1991, while the other data cover the period 1988 to 1990. Concentrations and fluxes are expressed in elemental units of* μEql^{-1} *and* gm^2y^{-1} *respectively.*

Concentrations

	Plynlimon	Mid Wales	UK range
Sulphate	18 9	20 - 40	<20 to >100
Nitrate	12.9	10 - 20	<10 to >40
Ammonium	16.7	20 - 30	<10 to >50

Fluxes

	Plynlimon	Mid Wales	UK range
Sulphate	0 76	0 6 - 0.9	<0.3 to >1 2
Nitrate	0.45	0.3 - 0.4	<0.2 to >0.5
Ammonium	0.58	0.3 - 0.6	<0.2 to >0.6

of the pollutant inputs of sulphate, nitrate and ammonium as wet deposition, they are relatively low for the UK in terms of concentrations, although the high annual rainfall volume means that the fluxes entering the catchment are relatively high (Table 2).

3.2 Chemical variations in streams draining undisturbed forest

The Plynlimon catchments experience rainfall with very variable chemistry while the streams exhibit a "flashy" flow response to rainfall inputs. Therefore, one might expect large variations in stream water concentrations that mirror the rainfall signal. This is not usually the case even for components such as chloride and ^{18}O, which are chemically unreactive (Figure 6; Neal & Rosier, 1990). This shows that the catchments have the ability to smooth the rainfall's variable chemical imprint to a very considerable degree. In other words, rainfall does not usually pass directly through the catchment to provide the major volume of water in the stream during the hydrograph response. During the major storm events, the rainfall signal sometimes influences the stream response and affects the response for the next few events.

In spite of the weak relationship between rainfall quality and stream chemistry, large fluctuations

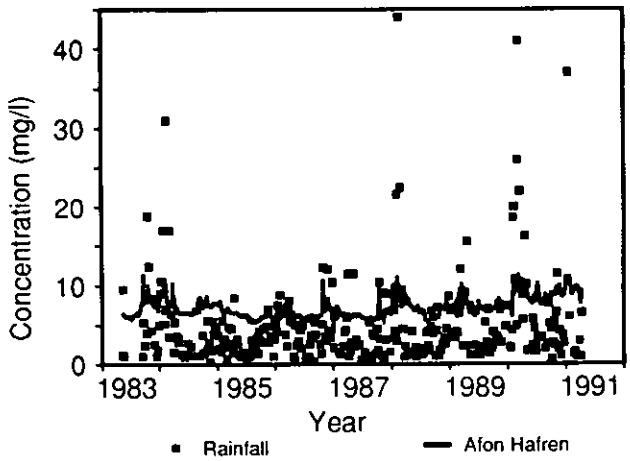


Figure 6 *Temporal variations in chloride concentrations*

in many chemical species occur because of hydrological variations (Table 3). Baseflow waters have higher calcium and silicon concentrations and alkalinities than the corresponding stormflow waters (Table 4, Figure 7). Stormflow waters, in contrast, have higher aluminium, yttrium, manganese, cobalt, nickel, beryllium and hydrogen ion concentrations than their baseflow counterparts (Table 4, Figure 7).

The major concentration changes occur at relatively low flows: at intermediate to high flows, concentrations remain either constant or decline as flow increases (Table 4, Figure 7). This difference reflects the large chemical gradients within the catchment. The soil zones, being organic and aluminium oxide/hydroxide rich, produce acidic, aluminium and transition metal rich soil water. The bedrock, consisting of weatherable and acid-soluble inorganic components such as calcite and layer lattice silicates (chlorite and illite), has the capacity to neutralise these acid waters and precipitate the easily hydrolysable transition metals and aluminium. Such reacted water degasses carbon dioxide on its passage to the stream and produces the characteristic low acidity, calcium and silica rich but aluminium and transition metal depleted base flow chemistry. During storm events, when the catchment soils have wetted up and groundwater tables are high, more water entering the stream is derived from the soil zone. With intense and long duration storms, more of the stormflow water is derived from the upper and most acidic soil layers and this change accounts for the declining concentrations of beryllium and aluminium at very high flow values.

Under baseflow conditions, water drains mainly from near the stream bank and from the groundwater areas. Variations in the bedrock composition lead to differences in the stream water

Table 3a *Average streamwater chemistries and ranges for the major elements in Plynlimon streams. All concentrations are in mgl^{-1}, except for pH (dimensionless), acidity and alkalinity (both μEql^{-1}). The mean pH values have been calculated from the mean of the hydrogen ion concentration.*

	Upper Hafren	Hafren	Upper Hore	Hore Pre - felling	Hore Post - felling
Na	3.95 (3.2-4 0)	3.90 (2 3-5.7)	3.89 (1.4-9.1)	4.31 (3.0-5.1)	4.05 (2.1-8.7)
K	0.16 (0.1-0.2)	0.20 (0 1-1.0)	0.13 (0.0-0 8)	0.17 (0.1-0.6)	0.30 (0.1-0.7)
Ca	0.46 (0 4-0.7)	0.76 (0.3-2 0)	0.89 (0.1-4.3)	1 3 (0.6-4.7)	1.1 (0.6-4.0)
Mg	0.61 (0.5-0.7)	0.75 (0.3-1.5)	0 64 (0.2-1.4)	0.85 (0.6-1.5)	0.80 (0.4-1.4)
SO_4	2.72 (2-4)	4.40 (2-12)	4 00 (1-10)	5.31 (3-11)	4 73 (3-11)
Si	1.3 (0.7-2.4)	1 3 (0.5-4.6)	1.0 (0.1-3.4)	1.5 (1.0-5.6)	1.1 (0.0-2.4)
DOC	1.7 (0.0-4.0)	1 8 (0.0-4.4)	1 6 (0.0-4.0)	1.5 (0.0-5.6)	1.6 (0 0-3 9)
NO_3	1.3 (0.5-2.8)	1.5 (0-6)	1.1 (0 1-4 6)	1.6 (0.4-3 3)	2.7 (0.3-4.7)
NH_4	0.02 (0.0-0.1)	0 02 (0.0-1.0)	0.01 (0.0-0 3)	0 04 (0.0-0.8)	0.02 (0 0-0.2)
PO_4	0.02 (0.0-0.1)	0 05 (0.0-1.0)	0.02 (0.0-0.2)	0.06 (0.0-0.2)	0.02 (0.0-0 2)
F	0.03 (0 0-0.1)	0.05 (0.0-0.2)	0.05 (0.0-0.2)	0.05 (0.0-0 2)	0.06 (0.0-0.2)
Cl	6.78 (5-10)	7.30 (4-12)	7.58 (4-20)	8.24 (5-19)	7.59 (5-22)
pH	4 85 (4.5-6.6)	4 46 (4.1-6.8)	4.74 (4.3-7 5)	4.84 (4.3-7.4)	4.76 (4 4-7 6)
Acid	129.2 (-36-301)	133.6 (-60-569)	135 1 (-29-385)	N/A (N/A)	172 4 (-14-360)
Alk	-13.3 (-30-43)	-22.0 (-63-69)	-11 1 (-53-218)	-0.8 (-47-197)	-12.0 (-47-175)

chemistries of the Afon Hafren and Afon Hore. The presence of calcite and lead/zinc sulphides in the Hore catchment leads to high calcium concentrations and measurable lead and zinc concentrations in the stream (Table 3).

Other differences in bedrock composition lead to contrasting behaviours of strontium and magnesium for the two catchments. Concentrations of lead and zinc in the Afon Hore are lowest under baseflow conditions. Thus either the parent sulphides in the bedrock are not oxidized to soluble forms or there is an unidentified ion exchange or solubility control in the groundwater. Differences in the bedrock are reflected in the correlation structure of the chemical data.

Many major, minor and trace components (Ca, Mn, Ni, Pb, Li, Al, Fe, Co, pH and alkalinity), together with the nutrients (NO_3, K, DOC, Br, I, B) show broad seasonal variations. This is best illustrated using time series plots of smoothed data obtained by taking a 'running mean' covering periods of four months. For the nutrient components, this seasonal pattern is linked to the biological changes through the year (Figure 8). For the remainder, much of the seasonality is linked to (1) the predominance of high flows during the winter periods and (2) the relative proportions of soil and groundwater contributions to the stream (Figure 9). The phases of the seasonal trends vary between species; peaks and troughs occur at different times each year and may even change from year to year. This

Table 3b *Average streamwater chemistries and ranges for the trace elements in Plynlimon streams (all concentration units are $\mu g l^{-1}$)*

	Upper Hafren	Hafren	Upper Hore	Hore Pre - felling	Hore Post - felling
B	4.1 (2.6-7.3)	4 8 (2-17)	4.3 (1-15)	5.5 (1-16)	4.9 (2-17)
Li	1 6 (0.9-2.3)	1.9 (1 0-3.3)	1.6 (0.6-2.7)	2 2 (1.5-3.0)	2.0 (1.1-3.1)
Sr	4.3 (3.7-5 2)	5.2 (2-11)	4.2 (1-8)	5.4 (3-9)	5.2 (2-9)
Y	0.36 (0.1-0.5)	0.34 (0.0-0.7)	0.29 (0.1-0.6)	0.30 (0 0-0.5)	0.30 (0 0-0.5)
Ba	2.1 (1-3)	3.6 (0-12)	3.2 (1-9)	5.1 (1-15)	5.3 (1-10)
Mn	19.0 (9-23)	40.8 (5-128)	21.9 (6-51)	34.9 (8-84)	40.1 (15-87)
Cu	0.4 (0-6)	2 2 (0-11)	2.7 (1-45)	2 8 (1-13)	2.8 (0-16)
Fe	115.2 (29-219)	98 4 (23-287)	83.3 (26-287)	74.1 (26-348)	89 1 (6-417)
Co	0.9 (0.4-1.2)	2.2 (0-17)	1.7 (0.0-3.0)	2.5 (0 0-4 1)	2 4 (0.1-4 5)
Zn	8.9 (3-14)	16 6 (3-116)	17 7 (4-74)	31.4 (4-56)	26 5 (2-68)
Al	165.8 (22-275)	347.1 (16-652)	362 3 (22-826)	342 9 (8-617)	438.5 (12-920)
Be	0.02 (0-0.04)	0.07 (0 0-0 2)	0.08 (0.0-0.2)	0 06 (0 0-0 3)	0.11 (0 0-0.2)
Ni	1.3 (0.4-4 2)	2.3 (0.0-5.5)	1 7 (0 2-3 4)	2.7 (0.0-4.3)	2.8 (0.4-5.6)
Pb	0.8 (0-2)	1.7 (0-21)	10.3 (0-25)	7.5 (0-18)	7.5 (0-14)
Cr	0.9 (0-5)	4.0 (0-51)	3.4 (0-28)	2 5 (0-40)	3 9 (0-40)
Br	19.4 (13-27)	22.1 (14-50)	21 1 (12-62)	20.6 (11-35)	24 0 (10-80)
I	1.1 (0.6-1.5)	1.1 (0.3-1.8)	0.9 (0.3-2.1)	0.8 (0.3-1 5)	1.1 (0.5-1 9)
Cond	41.0 (31-52)	44.5 (31-89)	46.6 (29-100)	31.7 (31-65)	51.6 (36-118)

illustrates that the rates of generation and consumption of the various elements are climate related but that no single reaction can describe all the changes occurring.

Under baseflow conditions, the stream water is saturated with dissolved CO_2. In contrast, stream waters under stormflow conditions are oversaturated by up to a factor of 8. Since the soil water and groundwaters are oversaturated 20 to 200 fold, major degassing occurs when the soil water and groundwater emerge into the stream. Under baseflow conditions, water volumes are sufficiently low and slow-moving for equilibrium to be reached: during stormflow conditions equilibrium with the atmosphere is not attained.

There are marked changes for some components following harvesting. While the seasonal patterns for nitrate and potassium persist for all the streams, there is a gradual increase in the concentrations following felling. For bromide, iodine, calcium and alkalinity less

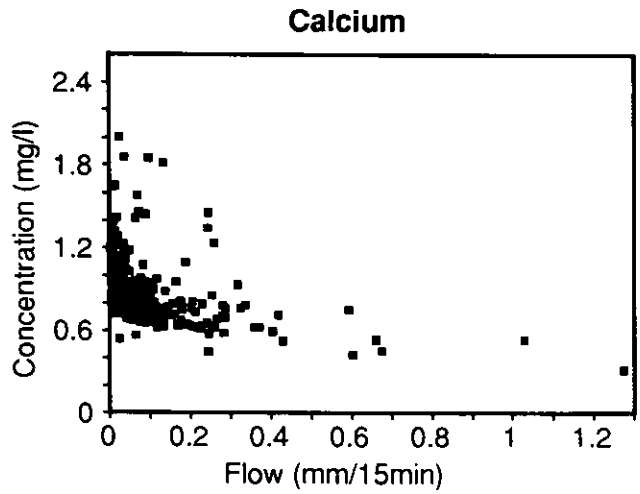
Table 4a *Average streamwater chemistries for the major elements in Plynlimon streams under baseflow (flows <0.02 mm/15min) and stormflow (flows >0.2 mm/15min) conditions. All concentrations are in mgl^{-1} units, except for pH (dimensionless), acidity and alkalinity (both μEql^{-1}). The mean pH values have been calculated from the mean of the hydrogen ion concentration.*

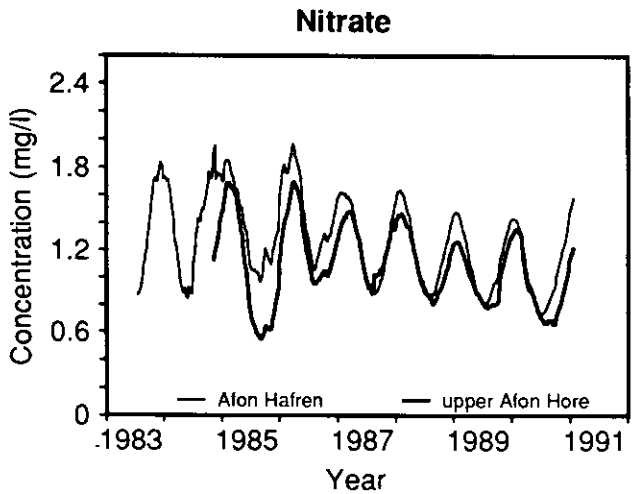
	Upper Hafren	Hafren	Upper Hore	Hore pre - felling	Hore post - felling
Na	3.59 (3.49)	4.00 (4.00)	3.85 (3.80)	4 29 (4.33)	4.21 (4.10)
K	0.11 (0.17)	0.13 (0 24)	0.10 (0 16)	0.16 (0.21)	0 19 (0.34)
Ca	0.62 (0.38)	1.02 0.71	2.51 (0.56)	2 83 (0.95)	2.43 (0.85)
Mg	0.66 (0 56)	0.82 (0.73)	0.83 (0.59)	1.14 (0.77)	1.05 (0.76)
SO_4	1.89 (3.04)	3.85 (4 73)	3.43 (4 16)	5.04 (5 53)	4 90 (4.65)
Si	2.07 (0 94)	2.05 (1.10)	1.72 (0 85)	2.29 (1.29)	1.72 (0.90)
DOC	0 48 (2.56)	0 83 (2.36)	0 89 (2.08)	0 79 (2.58)	0 92 (1 95)
NO_3	0.94 (1.26)	1.01 (1.72)	0.95 (1.24)	1.08 (1.87)	1.71 (2.67)
NH_4	0.02 (0.02)	0.02 (0.04)	0.02 (0.02)	0 02 (0.05)	0.02 (0 03)
PO_4	0.05 (0.02)	0.07 (0.07)	0.04 (0.02)	0.10 (0.19)	0.05 (0.01)
F	0.04 (0 03)	0 05 (0.06)	0 06 (0.06)	0 06 (0.09)	0 06 (0.06)
Cl	6.39 (6.48)	6.97 (7.46)	7.09 (7.56)	7 85 (8.07)	7.52 (7 79)
pH	6.31 (4.62)	5.94 (4.51)	6.84 (4.51)	6 97 (4.59)	6.53 (4 61)
Acid	123.7 (152 6)	126.6 (225.6)	150 6 (194.5)	N/A (N/A)	72.0 (-25 3)
Alk	26.4 (-27.3)	15.2 (-33.3)	95 9 (-33.6)	87 3 (-21.6)	50.2 (-54 8)

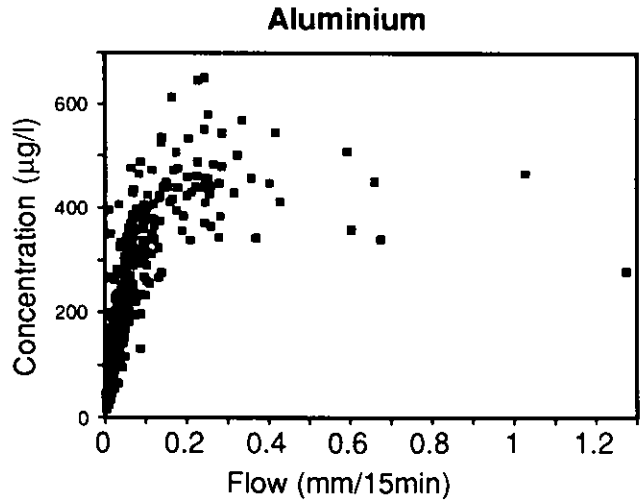
Table 4b *Average streamwater chemistries for the trace elements in Plynlimon stream under baseflow (flows < 0.02 mm/15min) and stormflow (flows > 0.2 mm/15min) conditions. The bracketed values are those for the storm flow samples. All concentrations are in μgl^{-1} units.*

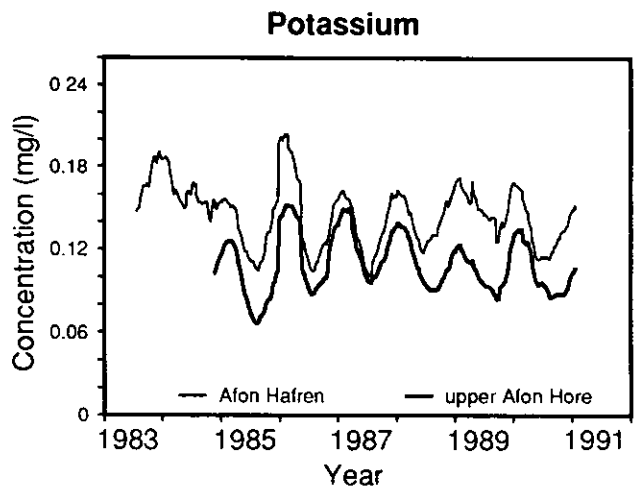
	Upper Hafren	Hafren	Upper Hore	Hore Pre - felling	Hore Post - felling
B	4.1 (4.5)	5.4 (5.0)	4 8 (4 4)	6.3 (6.1)	6.0 (4.9)
Li	1.7 (1.5)	2.0 (1.9)	1.8 (1.5)	2.1 (2.2)	2.0 (2.0)
Sr	4.3 (4.0)	5.5 (5 1)	5.4 (3.8)	6.9 (5.2)	6.6 (4.9)
Y	0.17 (0.41)	0.16 (0.39)	0.14 (0.33)	0.12 (0.38)	0.13 (0.34)
Ba	1 5 (2.2)	2.4 (4.0)	2.3 (3.3)	3 4 (5.6)	3.8 (5.5)
Mn	17.5 (16.5)	28 4 (43.7)	21.7 (20.9)	30.2 (38.3)	32.6 (40.4)
Cu	1 4 (0.4)	1.2 (2.6)	1.9 (2.8)	1.5 (2.5)	1.9 (3.8)
Fe	44.5 (150.9)	55.4 (114.9)	81.5 (87 5)	59.4 (96.4)	70.5 (95.8)
Co	0.7 (0.9)	1.4 (2.3)	1.2 (1.7)	1.4 (2.7)	1.4 (2.5)
Zn	5 2 (10.5)	11.3 (17.7)	11.1 (18.3)	17 2 (31.9)	13.3 (27.9)
Al	34.0 (236.1)	78.1 (456.2)	108.0 (469.9)	85.0 (487.3)	114.5 (558.1)
Be	0.01 (0.03)	0.03 (0.10)	0.03 (0.10)	0.04 (0 18)	0.03 (0.13)
Ni	0.9 (1.3)	1.6 (2.5)	1.3 (1.7)	1.9 (2.8)	2.0 (2.7)
Pb	0.7 (1 0)	1.8 (2.1)	3.4 (12.5)	3.5 (9.3)	2.2 (9.0)
Cr	0.8 (0.9)	4.6 (3.3)	3.9 (3.3)	3.6 (0.9)	4.6 (5.9)
Br	18.3 (21.4)	20.8 (23.4)	21.8 (21.7)	20.5 (21 4)	25.2 (25.5)
I	0.9 (1.3)	0.9 (1.2)	0 9 (1.0)	0.8 (0.9)	1.0 (1.1)

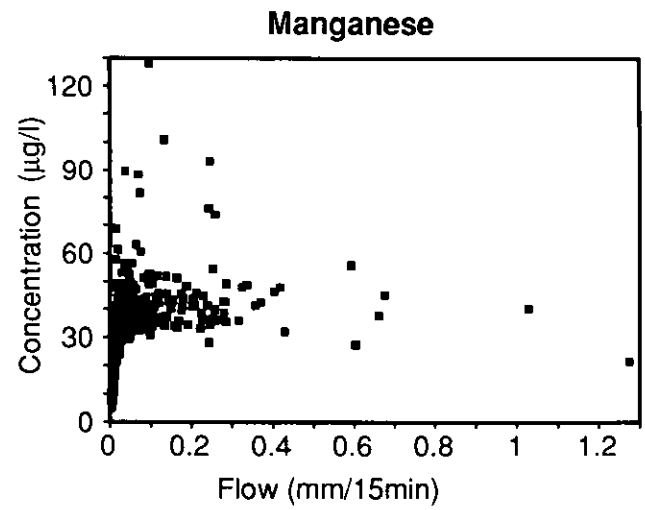
increase in the concentrations following felling. For bromide, iodine, calcium and alkalinity less pronounced changes occur: concentrations increase for the first two components but decline for the other two. Changes are also occurring for the other constituents but these are masked by the highly variable nature of the data. For this reason, and given that felling did not occur for the whole of the Afon Hore, a more elaborate means of assessing the effect of harvesting on the catchment scale was required. This is discussed in the next section.











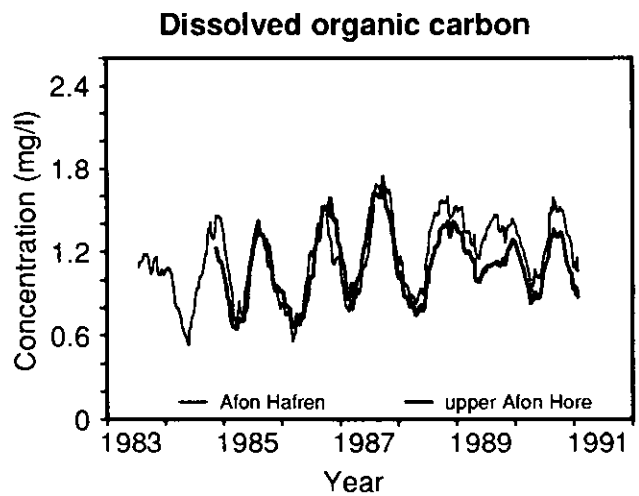
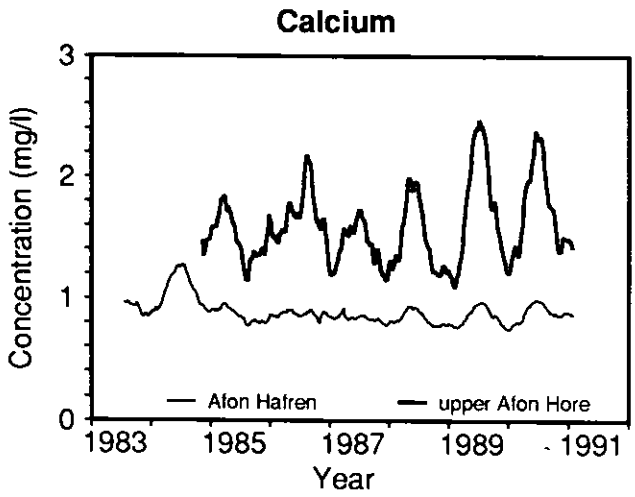
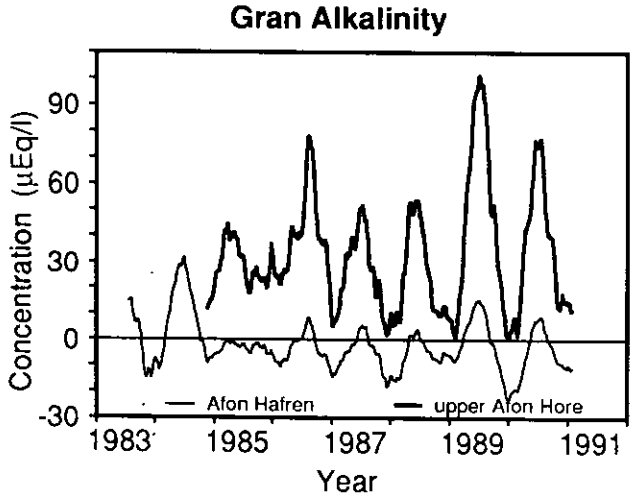


Figure 7 *Calcium, aluminium and manganese concentration relationships with flow for the Afon Hafren*

Figure 8 *Time series plots for smoothed concentration variations of nitrate, potassium and dissolved organic carbon in Afon Hafren and upper Afon Hore streams*





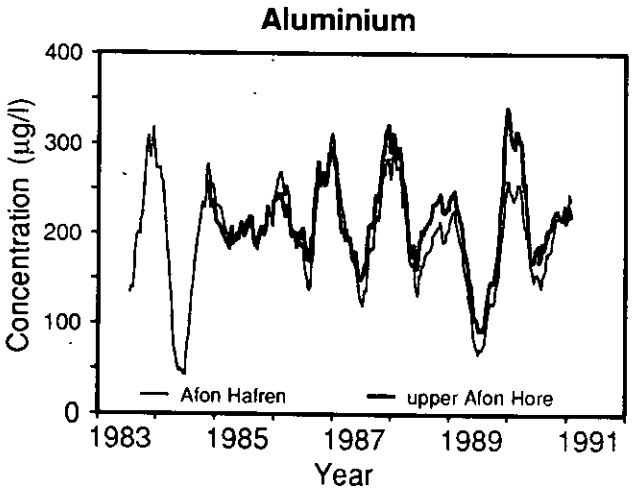


Figure 9 *Time series plots for smoothed concentration variations of calcium, aluminium and alkalinity in the Afon Hafren and upper Afon Hore*

4 The effects of conifer harvesting on stream water quality

4.1 A rationalised approach

Many of the chemical changes following harvesting are masked by the hydrologically induced variations in the streams. To identify the changes occurring, it was necessary to establish a pre-felling relationship between the upper and lower Hore. This relationship was then used, for the period after felling, to give an estimate of what might have happened had no felling occurred. This estimate will be referred to as the control response and is compared to the observed response. The control response was calculated as follows.

The stream chemistry associated with the area between the upper and lower sites on the Afon Hore, for the period prior to felling (C_{bf}), was determined using information on chemical concentrations at the two sites (C_u and C_l respectively). Allowance had to be made for the volumetric contribution of the lower portion of the catchment. The flow in the upper portion of the catchment is about half that in the down-stream area, both before and after felling. Consequently, the chemical composition of the felled area is given by the equation $C_{bf}=2C_l-C_u$. Note that this technique applies only to chemically conservative components. No direct analysis can be made for constituents, such as pH, which do not fulfil this requirement. Instead, a separate calculation was made for pH to overcome the non-conservative behaviour of hydrogen ions caused by acidity buffering by bicarbonate ions. The equation used sets the partial pressure of carbon dioxide for the averaged water to be three times the atmospheric value.

To provide a representative control response after felling (C_{af}), the chemistry of the felled area needed to be assessed for the hypothetical situation where no felling had taken place. This was achieved by fitting a linear relationship between C_{bf} and C_u ($C_{bf} = a.C_u + b$, where a and b are constants) for the period before felling. The chemical concentrations for the control, post felling, were determined using this equation with values of C_u post felling (C_u): $C_{af} = a.C_u + b$. In the exceptional cases where chemical variations were small and the linear correlation coefficient was low ($r^2 < 0.5$), C_{af} was taken as equalling C_u times the ratio of the mean values of C_{bf} and C_u before felling.

The final step in evaluating the results entailed providing a simplified description of the changes occurring. Large data scatter occurs throughout the study period due to the highly dynamic nature of the hydrochemical system under study. Because of this, direct comparison of the control and felled catchment data was extremely difficult. The effects of felling were dominated by the hydrologically induced variability of the system and compounded because the streams are not sampled simultaneously. To resolve this, time series plots were constructed for smoothed data by using a 'running mean' covering periods of four months.

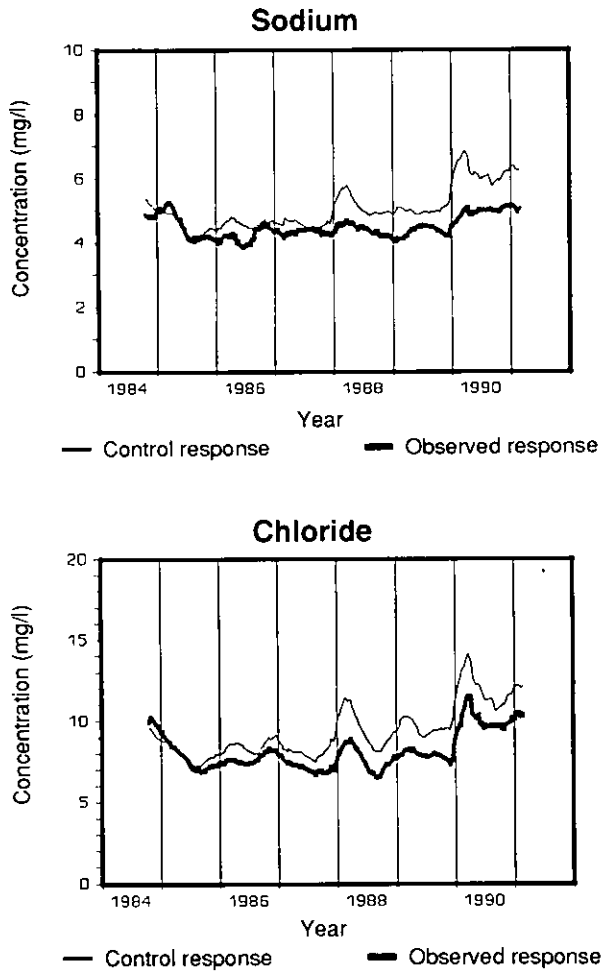


Figure 10 *Time series plots showing the effects of deforestation on stream water concentrations of sodium and chloride*

4.2 The sea salts

The stream response to major sea salt rainfall events has changed following felling. The stream values are reduced relative to the control response and over time the difference between the responses widens (Figure 10). Since the decline in flow is relatively small following harvesting, evapotranspirational variations cannot explain this difference. The results fit well with the notion that trees scavenge sea salt components as mist and dry deposition. They suggest that this enhanced deposition corresponds to an accumulation of an extra 20% of catch compared to the rainfall.

4.3 The nutrients

Biological activity within the soil affects the concentrations of nitrate, potassium, DOC, boron, barium, bromide and iodine in the stream water (Figure 11). Biological activity occurs at three levels (*cf* Stevens *et al.*, 1989; Emmett, 1989; Hughes *et al.*, 1990).

First there is decomposition of brash and stumps; this releases potassium and dissolved organic carbon with either a decrease or an increase in nitrate depending upon circumstances. Second, there is a break in the nutrient cycle as there is no longer uptake by the trees:

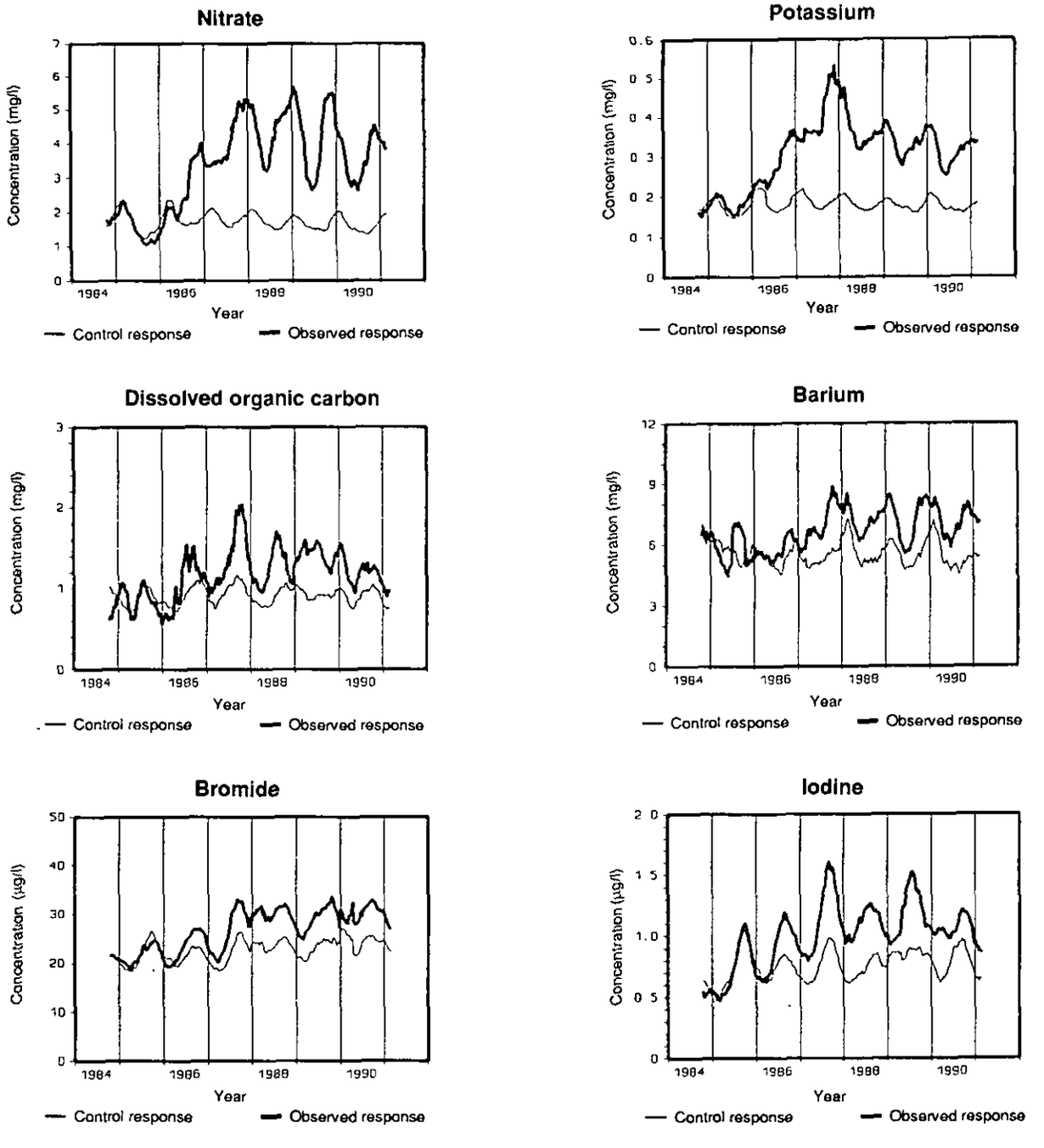


Figure 11 *Time series plots showing the effects of deforestation on stream water concentrations of nitrate, potassium, dissolved organic carbon, barium, bromide and iodine*

this leads to more potassium and nitrogen being available for leaching. Third, there is increased mineralisation of organic matter leading to the soil water being supplied with additional dissolved organic carbon and organic nitrogen. Nitrate supplies also increase because of the nitrification of ammonium. In the control area small seasonal cycles are observed.

Nitrate and potassium concentrations peak in the winter to spring period before felling and in the autumn to winter after felling (a three month phase shift). It seems that the presence of brash on the catchment limits vegetation development and this depresses uptake by the vegetation during the growth period. The breakdown of the brash is insufficiently rapid to remove nitrate by fungal and microbial processes.

For dissolved organic carbon, boron, bromide and iodine, summer or autumn maxima are observed. Following felling, there are marked increases in their concentration (typically about 50%) except for boron. There is no marked phase change after felling.

Variations in dissolved organic matter are linked to several processes: the general disturbance of the land leads to greater solution of organic components; hydrological conditions change so that more water is supplied from the organic-laden upper soil water; the micro-climate changes, with the loss of tree shade increasing soil temperature and thus the decomposition rate. For boron, bromide and iodine, the hydro-biogeochemical changes are complex and linked to the variations in the uptake and release rates by micro-organisms and the vegetation as well as to the rate of decomposition.

Although barium is not recognised as a biologically active nutrient, deforestation has led to increases very similar to bromide and iodine. This contrasts with previous research which pointed to barium behaving like calcium and strontium. These base cations are cycled within the vegetation and are released to solution from bedrock weathering. Thus it seems that barium, unlike calcium and strontium, is supplied to the stream more from the soil zone than from groundwater inputs.

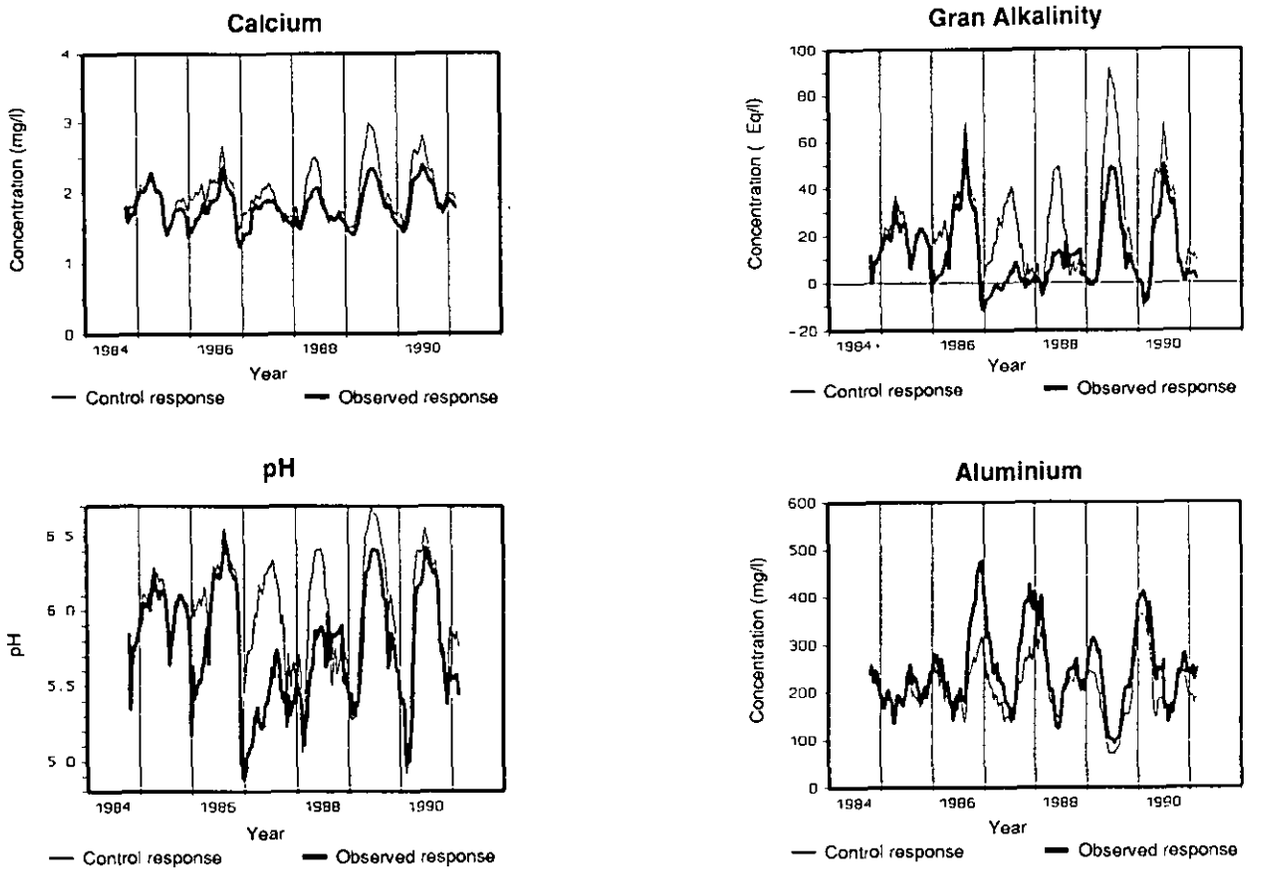


Figure 12 *Time series plots showing the effects of deforestation on stream water concentrations of calcium, Gran alkalinity, pH and aluminium*

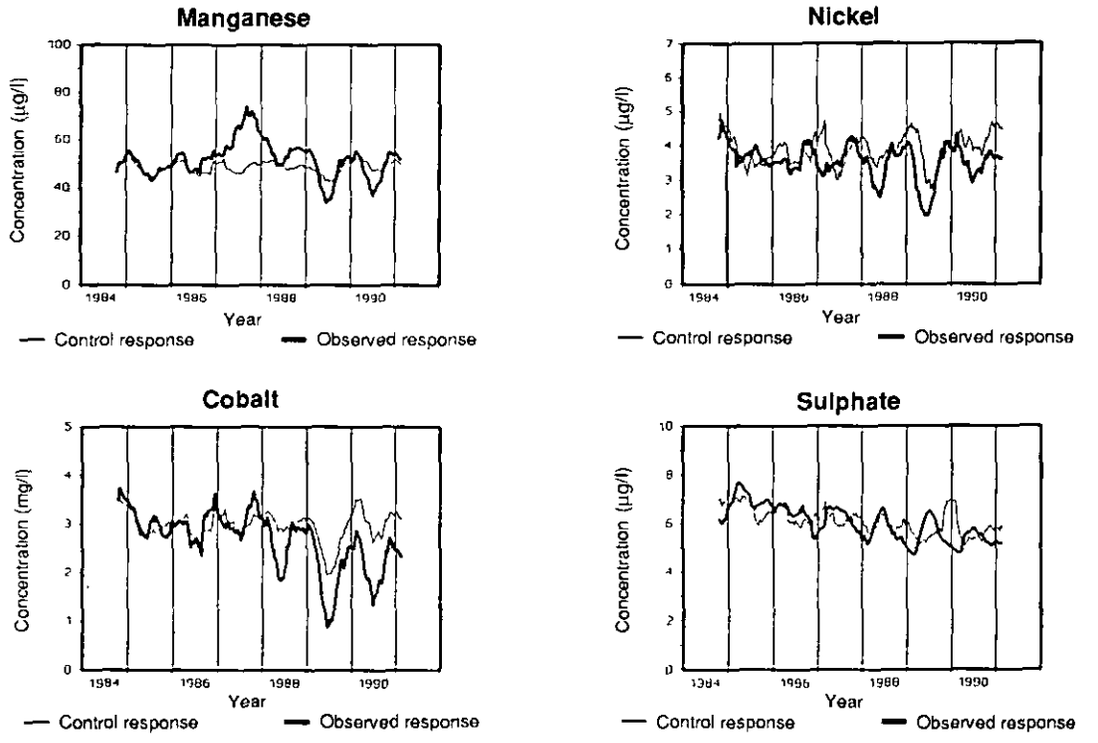


Figure 13 *Time series plots showing the effects of deforestation on stream water concentrations of manganese, nickel, cobalt and sulphate*

4.4 The inorganic components

The effects of tree harvesting on the inorganic components are as follows.

1 Calcium, alkalinity and pH. Seasonal patterns are considerably reduced for the first two years following harvesting: values remain close to the winter minima (Figure 12).

2 Aluminium. Seasonal cycling is enhanced for the first two years following harvesting: the main increases occur during the winter period when aluminium concentrations are at their highest (Figure 12). This indicates that there is a release of aluminium from the soils due to increased nitrate concentrations displacing aluminium from exchangeable cation sites.

3 Manganese. The seasonal patterns for manganese remain the same throughout the period except during the second summer following felling (1987) where concentrations were almost double normal values (Figure 13). This is despite land disturbance taking place over a three year period. This indicates that manganese supply to the stream is not uniform across the catchment. During this exceptional period, the main phase of harvesting occurred for valley bottom alluvium, peat and stagnohumic gley soils to the north of the main channel. Since this area is both manganese bearing and close to the stream, land disturbance most easily influences the stream water chemistry — further away from the channel, concentration fluctuations are reduced by damping processes associated with the hydrological and soil chemical processes.

4 Nickel and cobalt. The seasonal patterns remain with an accentuation of the summer minima. The reductions in baseflow concentrations show either that the water pathway supplying baseflow water has changed, or that other processes are operating in the stream during very dry periods to remove these components from solution (Figure 13).

5 Sulphate. There is a greater seasonality following harvesting: values are at their lowest during the winter period. This probably indicates a reduced sulphur store in the soil — sulphur scavenging will be reduced by loss of vegetation. However, there is also a decline in sulphate levels in the stream over time, for both the harvested and control situations (Figure 13). The general decrease may well correspond to a reduction in industrial emissions of SO_2 since the mid 1970s, although it must be remembered that 1983 and 1984 were very dry years and sulphate mineralisation was probably at its greatest.

6 All the other components. For these components, there are no visually discernable changes following harvesting.

4.5 Temperature

One of the important factors determining stream water vitality is temperature (Smith, 1980; Weatherley and Ormerod, 1990). Comparisons between the Afon Hafren and the Afon Hore show that there is not only a strong seasonal fluctuation in temperatures (mid-morning) but also a marked change following felling (the analysis above cannot be performed because of the 'non-conservative' behaviour of temperature). This change consists of two parts (Figure 14).

First, with deforestation, stream temperature rises during the summer to values higher than that for the streams draining the forested areas — but not the winter when values remain the same. The increase is typically about 4°C but sometimes it is as high as 9°C. Second, the rise in temperature seems to increase progressively each summer for the first four years following harvesting. These changes result from reduced shading of the stream by the forest (a feature most prevalent during the summer months when cloud cover is at a minimum), from warming up of the catchment, and from progressive removal of the trees shading the Hore stream.

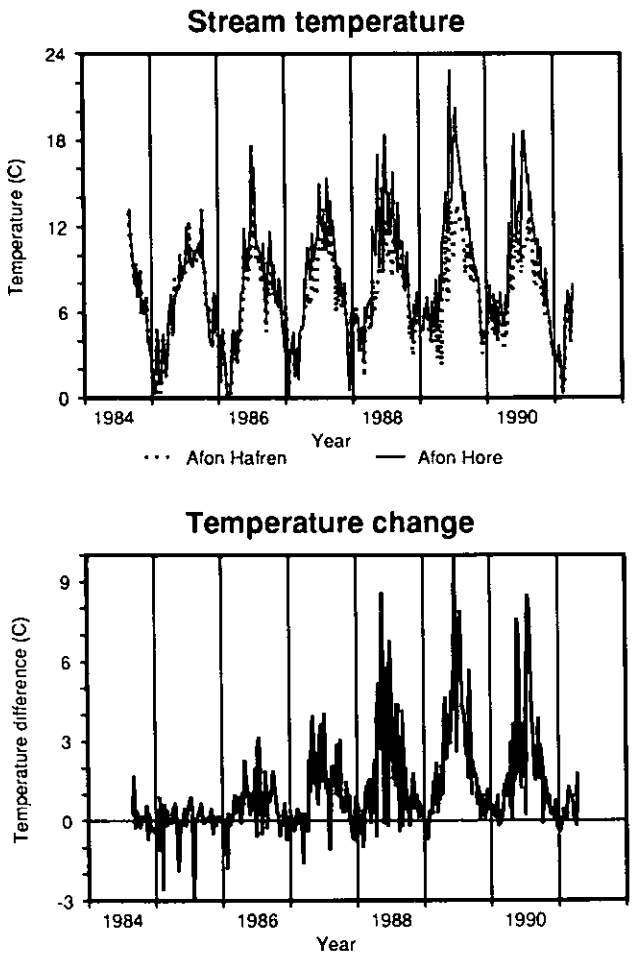


Figure 14 *Mid-morning stream temperatures for the Afon Hafren and the Afon Hore and the temperature differences*

There may, however, be an increased diurnal fluctuation — heat loss will be promoted on clear nights due to the lack of shading. The overall change results in near identical patterns to those observed at Plynlimon between moorland and forest streams (Kirby *et al.*, 1991). In terms of the biological status of the streams, the predominant effect of deforestation seems to have been to promote the return of mayflies within two years of harvesting (Dr J Gee, *pers. comm.*; Kirby *et al.*, 1991) although further work is required to establish whether this change remains on a long time scale. Such a return must be associated with temperature/light changes as all the other water quality parameters have deteriorated.

Further work is now being conducted by Dr Gee to establish the degree and longevity of this recovery. Deforestation has therefore led to an improvement in the stream environment during the summer months with respect to mayfly regeneration. However, this temperature change may hinder the return of fish, unless total inorganic aluminium concentrations reduce, due to temperature-induced changes in the aluminium speciation (see later in this report).

4.6 Near-surface run-off: the south2-Hore streamlet

The south2-Hore streamlet has run-off water characterised by acidic (pH range 4.3 to 5.0) and aluminium-bearing waters (range 248 to 566 μgl^{-1}) of low Gran alkalinity (range –10 to –52 μEql^{-1}). This is because the drainage waters come from a small hillslope area and the predominant water supply is from the soil zone and not from groundwater or a main stream bank area. Under prolonged dry spells, the streamlet dries up completely. Its chemical behaviour reflects the processes described in other sections. The salient features are as follows:

1 Na, Cl, Mg, Ca, Sr, Ba, Mn, Ni, SO_4 and Si. These constituents vary with inputs of atmospherically derived materials and with hydrological variations. Data from 1988 to 1990 indicate that (a) variations in the rainfall chemistry affect the size of the soil's chemical store, (b) the degree of evapotranspiration affects the salt content of the water and (c) major stormflow conditions allow direct input of water with a 'rainfall' chemistry.

2 NO_3, K, B, Br, I, Co, Zn, Cr and Li. For the nutrient components, plus — surprisingly — the four trace metal components, a cyclical pattern is observed which reflects the biological processes in the soil: see Figure 15 for examples. Throughout the study period, concentrations peak during the summer and late autumn periods, when biological activity is at its greatest. However, there seems to be an increase in concentration after felling, most evident for nitrate and potassium where concentrations more than double. Chromium concentrations decrease with time.

3 Alkalinity, pH, aluminium and DOC. For this group, concentrations are variable, with no discernable upward or downward trend until the time of tree harvesting. After felling, the waters become more acidic: alkalinity and pH decline. There is much scatter, but aluminium and dissolved organic carbon have probably increased following harvesting (see Figure 15).

4 The other components exhibit no distinctive pattern of behaviour although there is marked data scatter.

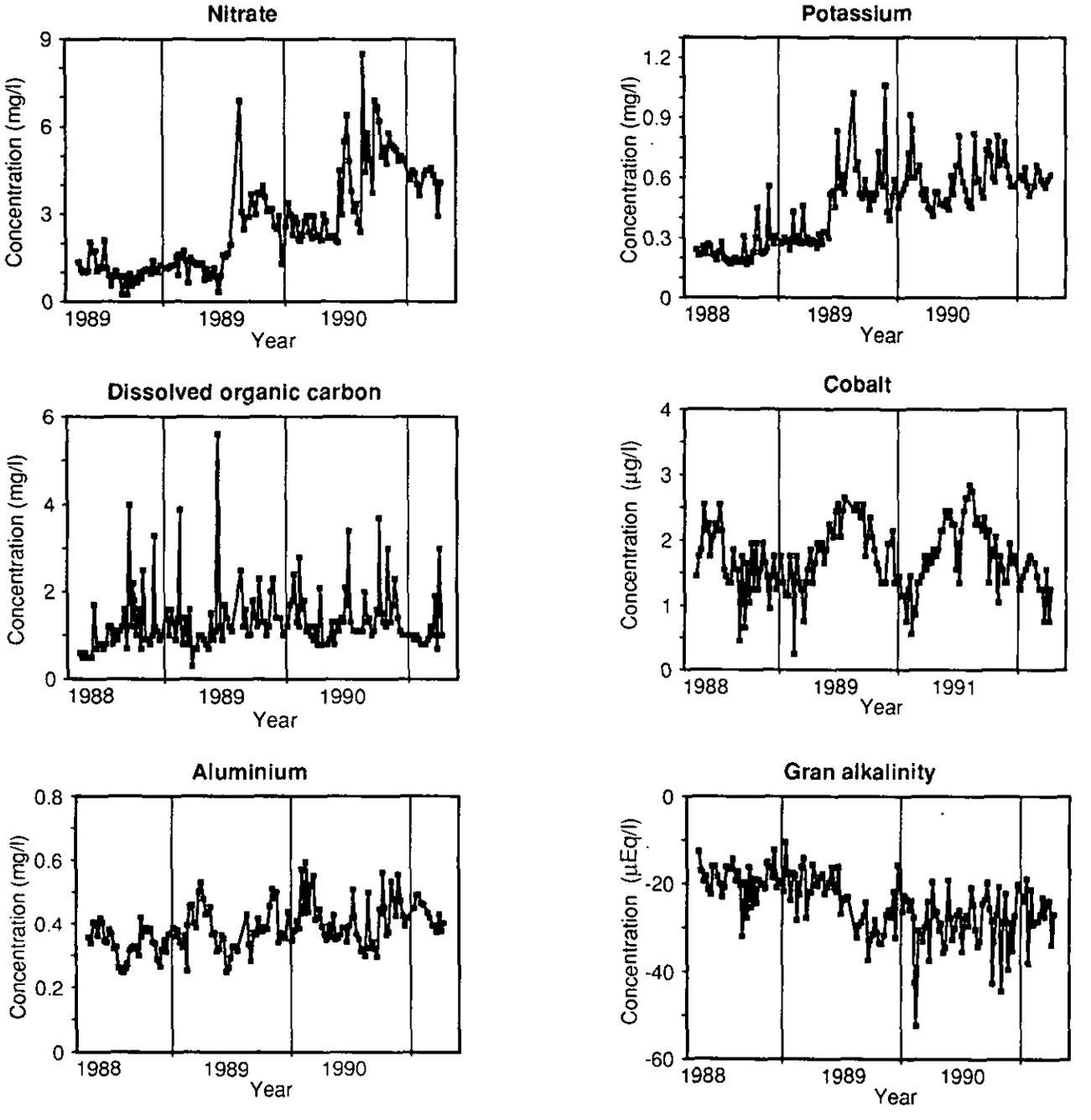


Figure 15 *Temporal variations in the concentrations of nitrate, potassium, cobalt, alkalinity, aluminium and dissolved organic carbon in south2-Hore stream water*

5 Chemical Budgets

5.1 Determination of input-output budgets

The annual input flux was calculated as the product of the mean annual concentration of bulk precipitation, weighted by the collected volume, and the annual rainfall, with a correction term allowing for dry and mist deposited materials. The correction assumes that there was a net input-output budget for chloride over the full monitoring period: dry and mist deposition amounts for the other elements were evaluated using the ion ratios to chloride in the cloud water. The annual output flux was determined using the chemical data from the weekly sampling programme together with the instantaneous flow values. As part of the determination, allowance was made for the distribution of flows between sampling times: an unbiased Beale's ratio estimator was used for the calculation.

5.2 Results

The results of the annual budgets for the full monitoring period and for individual years show three chemical groupings.

1 The components present within the bedrock and not supplied by the rainfall, i.e. Ca, Mg, SO_4, Ba, Mn, Fe, Zn, Al and Si, show a negative input — output balance: weathering processes provide a major flux to the stream. This imbalance varies for the different elements and there are variations between the subcatchments: the ranges (in kg ha^{-1}) are, respectively, 10 to 19, 3 to 9, 32 to 43, 0.02 to 0.06, 0.4 to 0.7, 1.3 to 1.6, 0.07 to 0.3, 6.2 to 7.6 and 19 to 25. In the case of sulphate, part of the imbalance may be associated with an underestimate for dry deposition as the calculations do not include a term for gaseous uptake by the trees. The observed imbalance is about twice the average value for dry deposition in this part of Wales, as estimated from atmospheric pollutant modelling studies (UKRGAR, 1990) — this calculated value is probably an underestimate as the trees enhance the uptake.

2 NO_3, which is predominantly supplied from the atmosphere rather than weathering sources, is approximately in input-output balance prior to felling (there are marked variations from year to year), but released to the stream following felling.

3 Sodium shows a net balance — it is mainly supplied from the atmosphere and undergoes little reaction on its passage to the stream.

5.3 Comparisons with other areas

The comparison of the budgets of the major elements with the mean results of other catchment studies in temperate and boreal regions (Avila & Roda, 1988) shows that the total losses of base cations in the Plynlimon catchments are slightly higher (1.0 to 1.4 keq ha^{-1} y^{-1}) than the average (0.8 keq ha^{-1} y^{-1}), while the silica budgets are the same (20 kg ha^{-1} y^{-1}), as a result of mineralisation in the bedrock. There is a significant loss of sulphate from the three catchments, indicating a long lasting acid impaction by atmospheric SO_2. The budgets of N species are balanced or positive when the forest is retained, showing that this acid impaction has had no considerable effect on the biological activity of the ecosystem. Nitrogen is exported from the catchment when the ecosystem is disturbed by felling activities.

6 Assessing the importance of water source contributions to streamflow

6.1 Rationale

The variations in stream water chemistry are linked, at a gross scale, to varying contributions from soil and groundwater inputs. To interpret fully the hydrochemical processes operating, the chemical hydrograph needs to be examined in sufficient detail to determine the dynamics of stream water supply. Unfortunately, water mixing relationships are difficult to assess for the streams. Although a neutral bicarbonate-bearing groundwater component is inferred from the

stream data, such an end member has not been sampled. Most chemical components which exhibit response to flow are chemically reactive and hence conservative mixing formulations cannot be used. Nonetheless, basic inferences can be made which provide some insight into the nature of the hydrological and hydrochemical processes operating. This is considered here by examining the chemical signals in the light of both weekly samples and continuous measurements of pH and conductivity.

6.2 Hydrograph separation: weekly sampling data

The starting point for assessing stream water mixing relationships is to examine concentration changes for the most variable but chemically conservative tracer, acid neutralisation capacity (ANC: the difference, in μeql^{-1}, between the concentrations of strong cations and strong anions in solution). The ANC equals the Gran titration alkalinity (μeql^{-1}) minus three times the inorganic aluminium concentration (μM).

The baseflow is assumed to be representative of the groundwater chemistry. Groundwater has not been directly sampled and average baseflow ANCs have been used to depict the end member value; 80 μeql^{-1} for the Afon Hafren, 200 μeql^{-1} for the Afon Hore (Neal *et al.*, 1990c). Within the soil zones, mean ANC differs for the grassland and forested parts of the catchment and areally averaged values have been used for the calculations (–104 μeql^{-1} and –93.3 μeql^{-1} for the Afon Hore and Afon Hafren, respectively). Under such circumstances the percentage hillslope (soil) ($\%_{hs}$) in a water sample of measured ANC (ANC_m) is estimated from the simple mixing equation

$$\%_{hs} = 100(ANC_m - ANC_g)/(ANC_{hs} - ANC_g)$$

where g and hs denote groundwater and hillslope water values respectively.

Results for this exercise show that as flow increases the proportional contribution of soil water from the hillslope increases and then levels off at high flows (Figure 16). Even under high flow conditions the groundwater component forms a very significant contribution to the total flow (20 to 60%).

The use of ANC only allows separation of the hydrograph into two end-members. Studying the behaviour of other chemical species provides a means of resolving further end-members, even though mixing may no longer be conservative. Different species show increased contributions in particular flow regimes, indicating when chemically distinct soil horizons begin to flow.

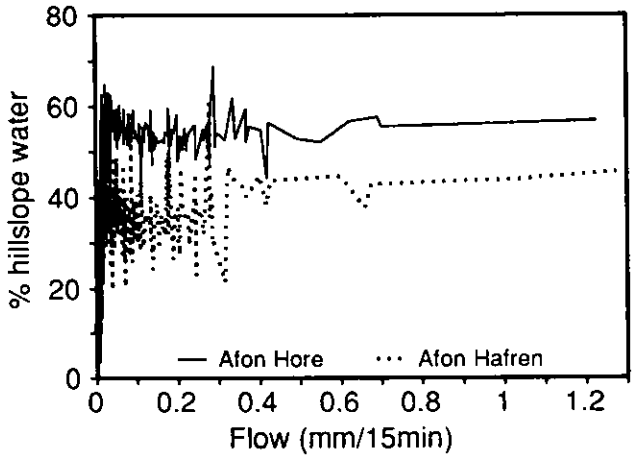


Figure 16 *The proportion of hillslope water contributing to flow - as assessed using chemical hydrograph separation techniques.*

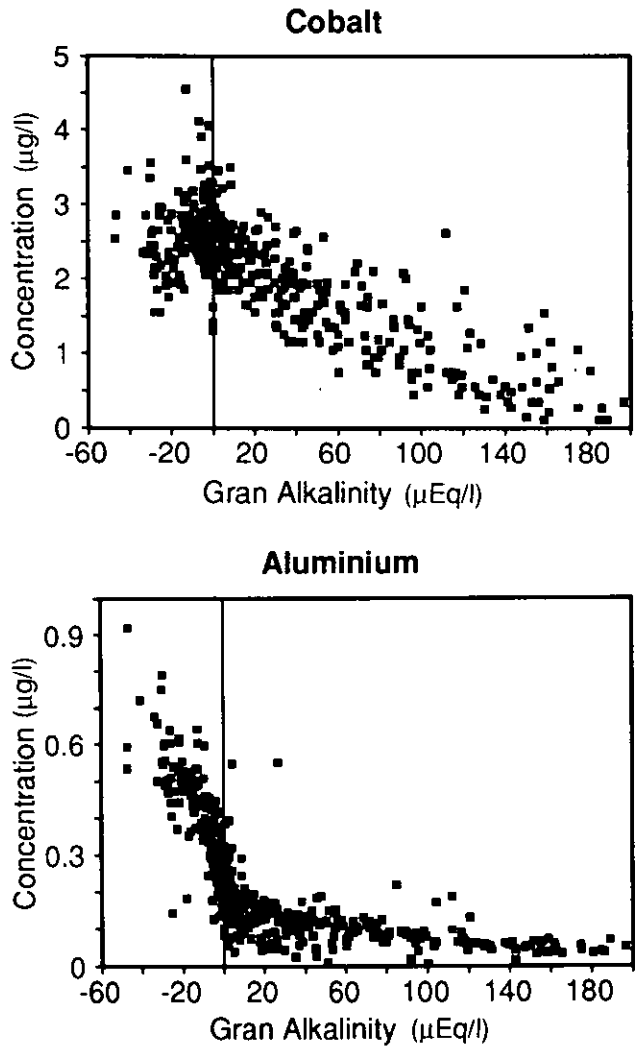


Figure 17 *Cobalt and aluminium concentration relationships with Gran alkalinity for the Afon Hore.*

Manganese, cobalt and nickel behave fairly conservatively except during drought conditions when they may be adsorbed onto the stream bed. The conservative-mixing nature of these components is most clearly shown when the concentrations are plotted against the acid neutralization capacity since a straight line relationship is observed (Figure 17).

Aluminium concentration changes take place over a wide range of flows. When concentrations are plotted against ANC, a curvilinear graph results (Figure 17). This behaviour is explained by non-conservative mixing involving aluminium solution/precipitation either in the stream or in the near stream bank areas (see the next chapter for details). At high flows aluminium is chemically conserved since the waters do not have the capacity for precipitating hydroxide or silicate phases. The upper and lower soil horizons have distinct aluminium levels and so a simple sub-division of the total soil contribution can be made. On this basis, under stormflow conditions, the 'O' horizon soil waters contribute 29 to 86 per cent of the total soil water component. The trace metals are of low concentration in the 'O' horizon. This explains why several trace elements decline in concentration under very high flow conditions.

6.3 Hydrograph separation: continuous data

Over the past three years, a considerable amount of data have been collected on changes in rain and stream water pH and conductivity. At present these data have not been fully evaluated given the complexity of the relationships being seen. Assessment has to be made on a storm-to-storm basis and the statistical and modelling work has yet to be fully established. Nonetheless, the early results show four main features:

1 The short-term changes in stream pH are very similar to those described for the weekly data. There is some hysteresis between the hydrograph rise and decline, but pH levels are generally quite closely linked with flow and this relationship does not change significantly with time.

2 There is a broad relationship between conductivity and flow on an event basis: as flow increases so too does conductivity. The rainfall signal is not usually seen within the stream hydrograph response. Such behaviour fits in well with our two component mixing model in which rainfall contributions are assumed to be small. However, for large

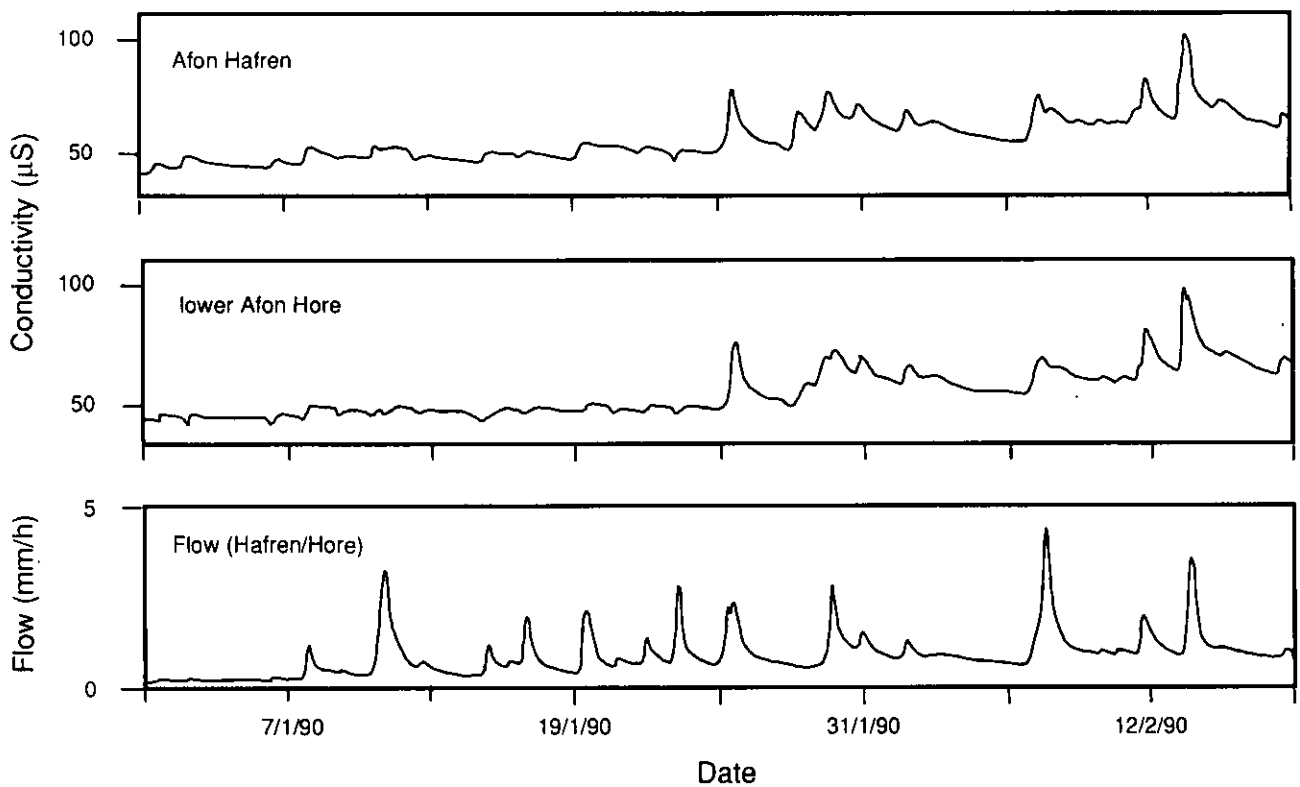


Figure 18 *Short-term conductivity changes in Afon Hafren and Afon Hore stream water.*

storms or when the catchment is very wet, the rainfall signal is, in part, rapidly transferred to the stream.

3 Despite the broad relationship between conductivity and flow, examination of a series of storm events reveals that the response to flow changes with rainfall inputs to the catchment (Figure 18). These changes indicate that the soil water end member does not have a constant chemical composition. When the catchment is supplied by quantitatively significant amounts of rainfall possessing either low or high salt contents, the soil water end member has a correspondingly low or high conductivity.

4 With the onset of a storm, the conductivity sometimes decreases before it increases (Figure 18). This pattern is most pronounced for the Afon Hore, although it is also observed on the Afon Hafren. This indicates the presence of a second groundwater end member for the Afon Hore and a differential behaviour between the Afon Hafren and the Afon Hore. Given the rapidity and the short lived nature of the response, the results indicate the input of a water from near the stream bank. Such differences could not be spotted with the weekly data as they are minor and occur over a very short period.

6.4 Conclusions concerning water mixing relationships

A broad explanation of the chemical variations within the Plynlimon stream waters can be formulated using weekly spot sample data, but the system is of sufficient complexity that more studies are required to describe mechanistically the detailed changes occurring.

The results indicate that the water supplied to the stream comprises a mixture of at least two types of groundwater and two types of soil water as well as rain water.

7 Chemical mixing, speciation and solubility controls for aluminium

7.1 Rationale

An important criteria for a healthy stream ecology is that inorganic forms of aluminium remain low (UKAWRG, 1988; Egglishaw *et al.*, 1986; Stoner and Gee, 1985). The environmentally harmful forms of aluminium within the streams are associated with trivalent aluminium, hydroxy-aluminium complexes and freshly formed polymeric hydrolysis products (Muniz & Leivestad, 1980; Baker, 1982; Driscoll *et al.*, 1980; Hutchinson & Sprague, 1987; Schecher & Driscoll, 1988). During the acidification process, concentrations of these environmentally harmful forms increase in the streams (UKAWRG, 1988; Whitehead *et al.*, 1988; Neal *et al.*, 1989b). Reliable estimates of the levels of the different aluminium complexes within solution are needed as some forms present in upland waters, such as the organic, fluoride and silicate complexes, reduce the harmful effect (e.g. Chappell & Birchall, 1988; Birchall *et al.*, 1989).

In this section the subject of aluminium solubility and speciation controls is addressed. This is provided to indicate the extent of environmentally harmful and inert levels of aluminium complexes in Plynlimon stream waters.

To achieve this objective, it has been necessary first of all to simplify the analysis as the speciation is influenced by a complex series of interactive factors such as hydrology, variable source area and temperature. This has been achieved by considering an averaged situation where the stream water is considered as a mixture of soil and groundwater end-members of fixed composition. Subsequently, the speciation of Plynlimon stream waters are examined to characterise the overall behaviour.

7.2 Modelling chemical speciation

The two-component mixing model used here is that developed from earlier studies at Plynlimon (Neal *et al.*, 1989a; Neal & Christophersen, 1989). During the mixing of soil and groundwater, microcrystalline gibbsite ($Al(OH)_3$) precipitates if the mixed waters become oversaturated with respect to this phase. No allowance is made for solution of microcrystalline gibbsite under the conditions where the mixed waters are undersaturated with respect to this

phase. Within the calculation, account is taken of aluminium complexation with fluoride, sulphate, hydroxide and silicate (AlF^{2+}, AlF_2^{1+}, AlF_3^0, AlF_4^{1-}, AlF_5^{2-}, $Al(OH)F^{1+}$, $Al(OH)F_2^0$, $Al(OH)F_3^{-1}$ $AlSO_4^{1+}$, $Al(SO_4)_2^{1-}$, $AlOrg^0$, $AlHOrg^{1+}$ $Al(OH)^{2+}$, $Al(OH)_2^{1+}$, $Al(OH)_3^0$, $Al(OH)_4^{1-}$) and $AlH_3SiO_4^{2+}$. A triprotic organic acid is used in the model (species H_3Org^0, H_2Org^{1-}, $HOrg^{2-}$ and Org^{3-}). Following mixing and on passage to the stream, water chemistry is modified by degassing of carbon dioxide and the extent of aluminium complexation varies in response to pH change. Partial pressures of carbon dioxide were set to constant values: 3 times the atmospheric value for the stream zone and 30 times for the soil zone.

The detailed speciation of aluminium is evaluated using the latest version of the programme ALCHEMI (Schecher & Driscoll, 1988). This involves using (a) output data, on inorganic aluminium, pH and bicarbonate, from the mixing model described above, (b) mean concentrations for the other components needed in the ALCHEMI computations (as determined from the hydrochemical data set) and (c) an average value for organically bound aluminium in the stream (25 μgl^{-1}: this value comes from unpublished analytical studies of Afon Hafren stream waters by Dr B. Reynolds).

7.3 Mixing model results

There is a strong, non-linear relationship between hydrogen ion and total dissolved aluminium concentrations for Afon Hafren stream water (Figure 19). At low to moderate hydrogen ion concentrations (0.2 to 15 μeql^{-1}) total aluminium concentrations increase sharply with increasing hydrogen ion concentration: at higher hydrogen ion concentrations (20 to 70 μeql^{-1}) total aluminium concentrations increase only moderately with increasing hydrogen ion concentration. This pattern is well characterised by the mixing model described above.

Four effects produce the curve shown in Figure 19. First, microcrystalline gibbsite is precipitating at low hydrogen ion concentrations — this produces a cubic relationship between trivalent aluminium and hydrogen ion concentrations. Second, trivalent aluminium is supplemented by the presence of aluminium hydroxide and fluoride complexes at low hydrogen ion concentrations. Third, on entering the stream, the mixed waters degas carbon dioxide and this causes an increase in pH but no change in the total aluminium concentration. The pH change is most noticeable at the lowest hydrogen ion concentrations when bicarbonate buffering of acidity is most important. The first term gives the main structure to the upper portion of the curve while the other two terms control the lower portion. Fourth, at moderate to high hydrogen ion concentrations (20 to 70 μeql^{-1}), both hydrogen ions and total aluminium are unreactive and a simple linear mixing pattern results — carbon dioxide degassing does not significantly change the pH while aluminium hydroxide precipitation does not come into play.

The analysis shows the following:

1 The relative concentrations of trivalent aluminium and aluminium complexes with hydroxide, fluoride, dissolved organic matter and silicate are all significant for the water end-members and their mixtures: they comprise over 15% of the total aluminium in solution in part of the pH range (Figure 20): aluminium sulphate and aluminium hydroxy fluoride complexes make up less than 1% of the total aluminium concentration.

2 The highest concentrations of trivalent aluminium occur at the lowest pH considered; concentrations decline to insignificant levels at pH greater than 5.

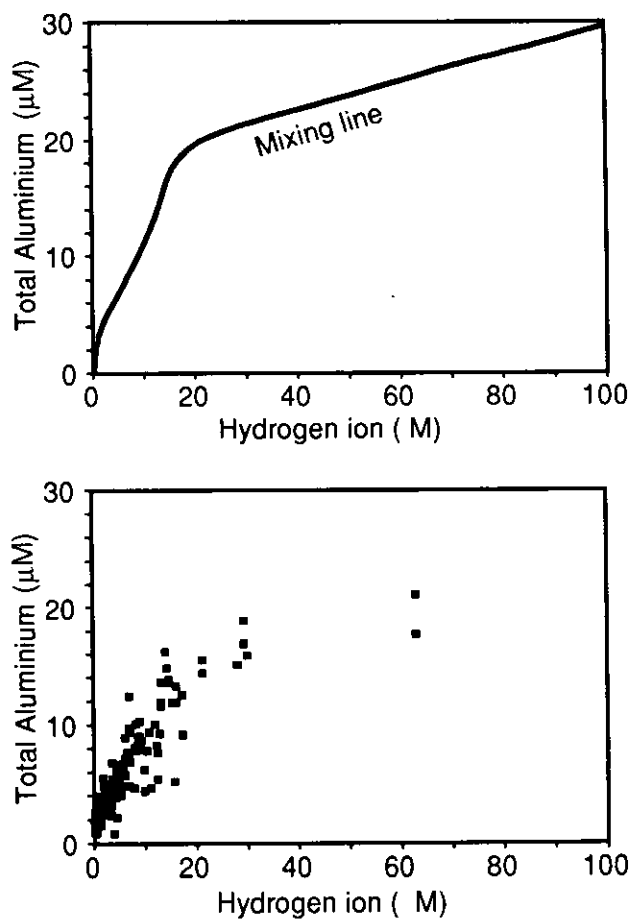


Figure 19 *Concentration relationships between total aluminium and hydrogen ions for the Afon Hafren: observed and modelled values*

3 At intermediate pH a mixture of complexes occur in similar proportions.

4 In the higher pH range hydrolysis of trivalent aluminium becomes more prevalent and aluminate starts to dominate.

5 The proportions of the various aluminium complexes vary markedly as a function of temperature, although the same basic patterns are maintained (Figure 20). This variation is a result of the pronounced temperature dependence of the equilibrium constants for aluminium hydrolysis and is most important for the aluminate ion ($Al(OH)_4^-$). Consequently, the highest deviations occur at the highest pH.

7.4 Field results

Analysis of the stream water data show similar features of aluminium complexation described in the previous section. The results show:

1 Trivalent aluminium predominates at low pH;

2 Although most fluoride is bound to aluminium at low pH, there is insufficient total fluorine present to complex the large amounts of aluminium present at low pH;

3 Aluminium hydroxide complexation increases in importance at intermediate to high pH;

4 Trivalent aluminium and aluminate, while important at intermediate pH, do not dominate the system in this range;

5 While organic aluminium concentrations vary with pH, the variation is small — at low pH the organic acids are essentially undissociated, while at high pH trivalent aluminium is extremely low.

The field results exhibit considerable scatter for the various aluminium species (Figure 21). This scatter represents the variability in the stream water chemistry and temperature. Temperature related scatter occurs for the higher pH waters: the greatest temperature dependent equilibrium constants are for those species most prevalent at higher pH; baseflow occurs both during the summer and winter periods and therefore temperature is at its most variable (2 to 20 °C).

7.5 Deforestation effects

The results indicate that the environmentally harmful forms of aluminium will increase in the

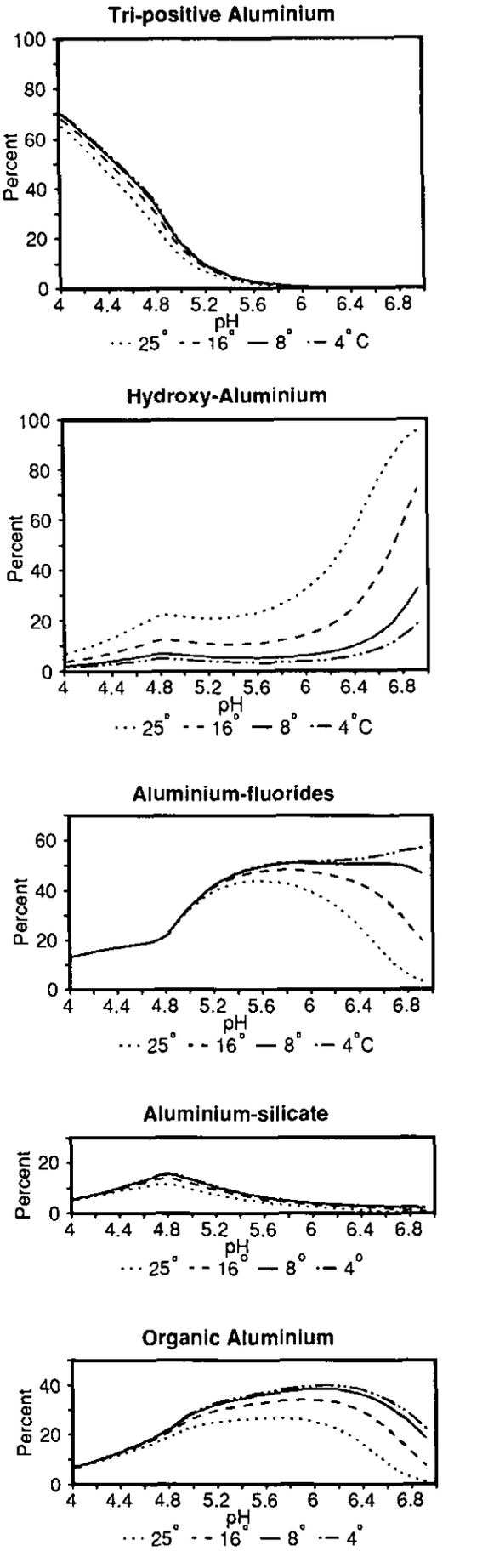


Figure 20 *Aluminium speciation relationships for Afon Hafren stream waters - two component mixing model values*

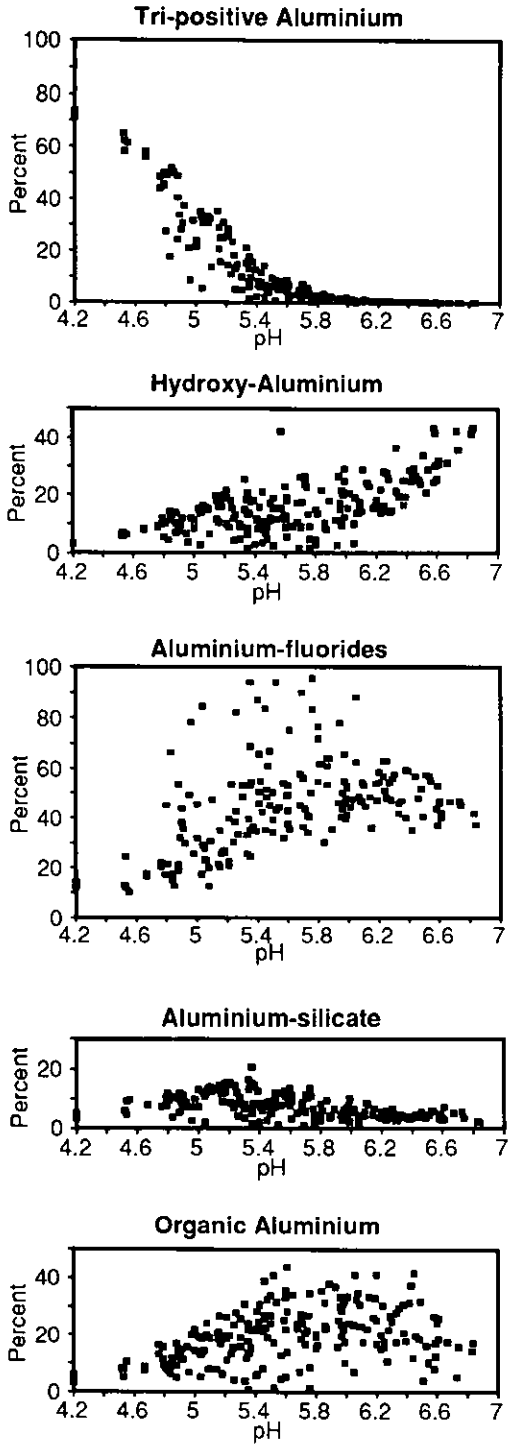


Figure 21 *Aluminium speciation relationships for Afon Hafren stream waters - field results*

stream following deforestation: silica, fluorine and dissolved organic carbon concentrations will not increase sufficiently to complex the increases in total aluminium. Moreover, as stream temperature increases in response to deforestation, a higher proportion of the environmentally harmful forms of aluminium will be present in the stream — this is a consequence of the changes in the equilibrium constants for the aluminium-hydroxide complexes with temperature.

7.6 Aluminium regulation within Plynlimon soils

One of the features of the acidification research has been the assumption that the soils undergo simple cation exchange reactions and that the transfer of acidity and aluminium to the stream are linked to the movement of 'mobile anions' such as sulphate, nitrate and chloride. However, hydrogen ions and trivalent aluminium concentrations conform neither to the theoretical cubic relationship nor the associated temperature dependent co-relationship (Neal *et al.*, 1988, 1990a).

These findings are reinforced by hydrochemical features associated with the catchment scale perturbations. The simple ion exchange equations commonly employed, indicate that all the base cations increase as the anion concentration increases (Reynolds *et. al.*, 1988; Neal *et. al.*, 1989, 1990a); this is not the case with calcium and sodium as their concentrations decrease in the stream under high flow conditions following felling. Furthermore, the sea salt events which occasionally characterize the stream chemistry are not possessed of abnormally high acidity and aluminium levels in contradiction to the simple cation exchange formulation. Consequently, one of the most important features of the Plynlimon study has been the recognition that despite over a decade of intensive research world-wide, the mechanisms determining hydrogen ion and aluminium mobility, remain obscure.

8 Modelling Studies

8.1 Modelling background

Modelling work has been undertaken for the Plynlimon catchments to describe both short- and long-term variations in stream water quality. These modelling studies constituted part of the Royal Society's *Surface Water Acidification Programme* and the European Community's *Encore* project. The findings are briefly summarised and the future direction of work considered.

8.2 Short-term modelling studies — applications of TOPMODEL

Modelling studies of chemical changes occurring in the Afon Hafren and Afon Hore during storm events have centred on the application of a semi-distributed physically based hydrological model — TOPMODEL (Beven & Kirkby, 1979; Beven *et al.*, 1984). This model was chosen because it takes into account the catchment feature most important for determining the hydrological response — the topography. Catchment topography is represented in the model by means of an index function (Figure 22). Areas with a high contributing area and a low slope are likely to be both wet and important hydrological sources.

The work has focused on trying to link the hydrological and the chemical response of the stream on an episodic basis. TOPMODEL was adapted so that the contributions to the stream from different soil horizons could be estimated. These results were then compared with the chemical separation between soil and ground waters using continuously monitored chemical signals. TOPMODEL estimates two components of streamflow — (1) quickflow, thought to move by macropore-flow, overland-flow or piston displacement and (2) a subsurface flow. The modelling results compare well with the chemical signals but they indicated that the quickflow component has a composition different from the soil and rainfall chemistry (Figure 23).

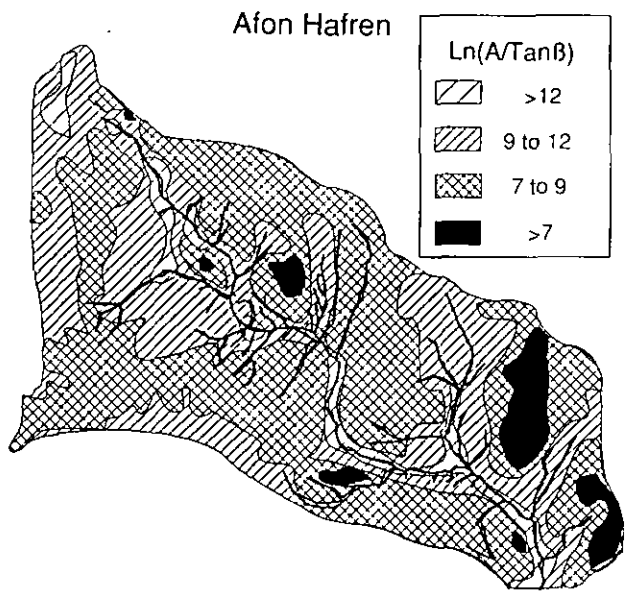


Figure 22 *TOPMODEL index function variations for the Afon Hafren*

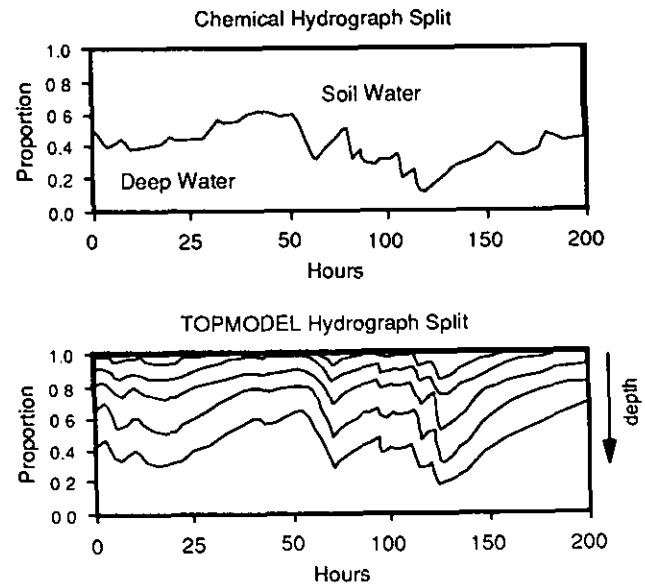


Figure 23 *TOPMODEL predictions of mixing relationships for the Afon Hafren — comparison with chemical mixing results*

8.3 Long-term modelling studies — applications of MAGIC

MAGIC (a Model of Acidification of Groundwaters In Catchments) is a chemical model which uses equilibrium and mass balance equations to describe catchment input-output relationships. Detailed descriptions of the conceptual basis of the model are documented in Cosby *et al.* (1985a,b) and Jenkins *et al.* (1990).

Early attempts to model the forestry system were confined to a one-box application of the MAGIC model. This application showed:

1 acidic oxide deposition results in stream water acidification for both moorland and forested areas: the degree of the acidification increased with increasing acidic oxide deposition;

2 the introduction of trees enhanced the acidification effect by increasing the scavenging of atmospheric pollutants;

3 harvesting trees in an environment polluted by atmospheric deposition results in a reduction in the stream acidity and an increase in stream pH (provided that biological effects are small — i.e. nitric acid is not generated);

4 afforestation does not cause acidification unless there are pollutant inputs to the catchments.

Work over the past two years at Plynlimon and elsewhere has shown the importance of hydro-

logical flow pathways and the biogeochemical functioning of catchments in determining stream water chemistry. The identification of the dominant flow pathways is important in that such processes determine the fluxes of chemicals from different parts of the catchment. The biological processes are particularly important when dealing with systems such as Plynlimon which have been afforested and deforested.

Previously, empirical relationships between biological diversity and mean water quality values were obtained for a wide range of streams (Ormerod *et al.*, 1988). The relationships relied on there being a high correlation between the mean and the extreme stream water quality for those chemicals that determine toxicity levels (Weatherley & Ormerod, 1991). These relationships have been used with water quality predictions from the earlier versions of MAGIC to assess the environmental impacts (Ormerod *et al.*, 1988). However, this approach is an over-simplification and future aims must be to (1) assess the changes in baseflow and stormflow chemistry, (2) predict the frequency and duration of acidic episodes and (3) link the information generated under items (2) and (3) with more detailed biological indices. Such a development depends upon providing more detailed and reliable models to achieve a more thorough understanding of the relative effects of changed chemistry during episodes and baseflow.

To reflect the importance of hydrological flow pathways and episodicity in determining stream water chemistry, a two box version of the MAGIC model has been applied to the grassland areas at Plynlimon — a prelude to the more difficult step of describing the impacts of afforestation and deforestation on stream biota. Use was made of data collected by the Institute of Terrestrial Ecology for a semi-natural moorland stream (Afon Gwy). The results from MAGIC showed that the long-term predictions are sensitive to flow routing and to the representation of the sulphur store dynamics.

The long-term changes in episodic stream chemistry variations were assessed by applying the chemical speciation model described earlier in this report (ALCHEMI) to the results from MAGIC. The results indicate that reduced anthropogenic sulphur deposition will not lead to as rapid a recovery in aluminium concentrations as was previously thought. Two methods, for use with critical load evaluation of ecological stress, have been developed and these are shown in Figure 24.

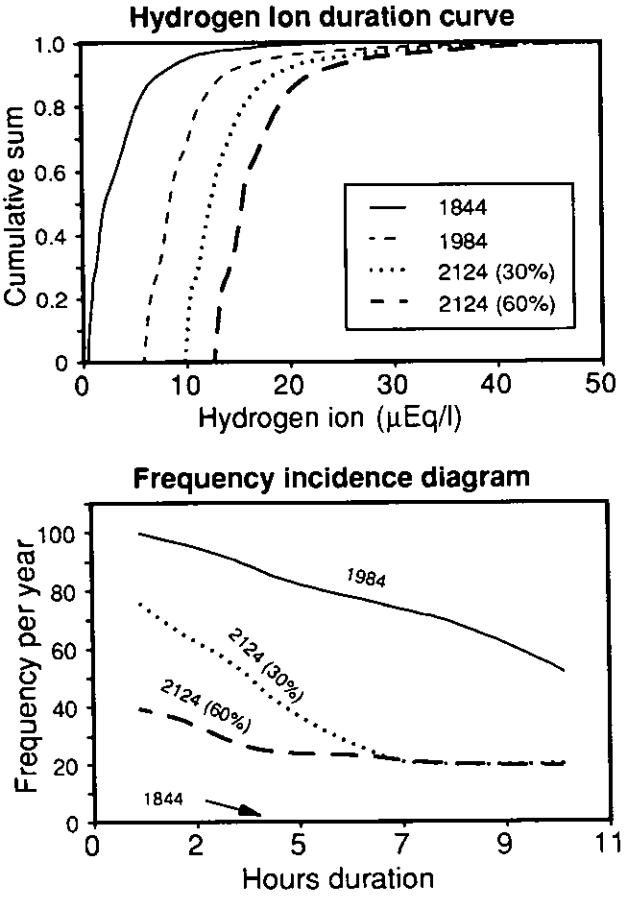


Figure 24 *MAGIC model assessment of the frequency of acid events for the upper portions of the River Wye with predictions for future scenarios involving different atmospheric pollutant loadings of sulphur*

8.4 Future modelling work

In order to describe the affects of afforestation and deforestation, it is essential that allowance is made for the changes in the soil water chemistry, and that flow pathway reactions are identified. Additional monitoring is required to establish the length of time it takes for the re-establishment of a catchment equilibrium to occur following deforestation. Further, it is essential that the rates of cation uptake by the vegetation and the rates of depletion of the soil's base cation store be established as these provide important controls on the rate and extent of acidification.

Although trees are known to capture particles rich in base cations and to cycle base cations from the lower parts of the soil to the canopy, these inputs are not measured. Present MAGIC predictions are critically controlled by the estimated chemical inputs, yet the only data available are from rainfall devices which do not include the scavenged and cycled sources.

More consideration needs to be given to the description of cation exchange reactions and sulphate adsorption. It is essential that allowance is made for exchangeable hydrogen as well as exchangeable aluminium and that the long-term sulphate stores in the soil are assessed.

By combining modelling and field work, hypotheses on the dominant hydrochemical and hydrological pathways may be tested. The object of this exercise would be to provide a simple description of the catchment which reflects the major stream chemistry characteristics. The simpler the model the easier it will be to produce a regionalised perspective.

9 Water resource implications

9.1 Plynlimon findings in perspective

The results of the Plynlimon study indicate that water quality will, in general, deteriorate for at least two years following harvesting and that after this time some improvement will occur. For some components such as the nutrients, results fit in well with previous observation (Likens *et al.*, 1970; Lawrence *et al.*, 1987, 1989; Stevens & Hornung, 1987; Hornung *et al.*, 1989; Adamson & Hornung, 1990; Reynolds *et al.* (*in press*), Dr. R. Harriman, *pers. comm.*; Johnson, 1991) while in other cases (e.g. aluminium, hydrogen ions, bromide and manganese), results are either different, in some way, or unexpected: sediment loadings are also adversely influenced (Appendix 3). The Plynlimon findings provide the most pronounced acidification effects on stream water quality seen within the UK studies. On a positive note, there has been some ecological benefit of deforestation: decreased shade and increased stream temperature have allowed the return of mayflies to the stream channel.

The Plynlimon system is perhaps atypical of the UK uplands in that the baseflow alkalinity is relatively high, a result of calcium carbonate in the bedrock (Neal *et al.*, 1990a,b; Reynolds *et al.*, 1986). For a system of lower baseflow alkalinity, where storm flow water chemistry is of marginal quality, felling activity may, according to circumstance, introduce a short-term adverse effect on stream ecology. This situation will either be made worse by a more intensive or extensive harvesting programme or made more benign by a gentler and more thoughtful approach. Some comfort can be taken from three features of the Plynlimon results. First, water quality recovers from deforestation within a few years. Second, the widespread belief that episodic inputs of rainfall enriched in sea salts necessarily produce high acidity and aluminium-bearing stream water responses seems unfounded: hydrological bypass mechanisms come into play. Third, not all catchments show the same behaviour.

However, little comfort can be taken from longer-term modelling work which suggests a second and more potent phase of acidification following replanting (Jenkins *et al.*, 1990). This point becomes most poignant for the other deforestation studies in the UK where nitrate increases are balanced by base cation releases rather than acidity and aluminium generation: the catchments rather than the streams are presently undergoing enhanced acidification. To quote Jenkins *et al.* (1990) "Comparisons of future forest management strategies in conjunction with likely deposition reductions indicate that, in sensitive areas, replanting of a felled forest without treatment of the soil by addition of base cations should not be undertaken even if significant deposition reductions are realised".

Regarding the extent of the harvesting effect on stream waters at Plynlimon, the effects would probably have been much more pronounced if a more aggressive or extensive harvesting policy had been employed. For example, nitrate and potassium concentration increases of three or more times the levels observed in this study have been seen in a more rapid felling exercise, albeit at a plot scale (Adamson & Hornung, 1990). The effects of tree harvesting will depend upon the soil types, the size of the exchangeable base cation pool, the soil distribution and the hydrological pathways. The Plynlimon soils comprise a variety of acid-soil types and the changes seen are an integrated effect.

At first sight, the effects of tree harvesting on stream ecology are negligible — after all, the Afon Hore storm flow water has been unsuitable for fish throughout the study period. However, the increase in aluminium following felling may have made the situation worse by increasing the length of stream which is adversely affected.

The Plynlimon results provide the first clear indication of deterioration in baseflow water quality upon harvesting. While this is probably of little or no effect at Plynlimon, it is an

important flag by which to highlight a potential environmental risk for more marginal situations.

9.2 Protecting the upland environment

The effect of conifer afforestation and acidic oxide deposition in the UK uplands has been in some cases to increase the acidity and the aluminium concentrations in streams, to acidify the catchment soils and to increase the sediment loads. The summation of these effects is a cause of environmental deterioration in the stream environment of parts of the British uplands. Improvement in the environmental quality of the upland streams where biological deterioration has occurred (be they forested or not) will primarily require long-term containment and reversal of the acidification process. For the present, this study addresses a major concern over deforestation: there may well be a temporary increase in acidity and a second and more potent phase of acidification if new trees are planted. During deforestation, in environmentally sensitive water resource (amenity and water supply) areas, an important objective will be the lowering of organic carbon, bromine and possibly manganese levels in public water supply areas.

To protect the sensitive parts of the upland environment in relation to forestry, there seem to be only a limited number of strategies available as many proposals such as bank-side clearance seem to be ineffective (Hornung *et al.*, 1990). These strategies include:

1 Prevention of new acid sensitive areas from being afforested and prevention of reafforestation of acid sensitive areas unless ameliorative schemes are included within the proposals.

2 Improved forest management practices/ implementation of presently recognised good-forestry practice (e.g. to limit sediment transport).

3 Rapid establishment of vegetation following harvesting/land-disturbance to minimise the releases of nitrate to the catchment soils. This is important since the rate of recovery of stream water aluminium concentrations following felling/land-disturbance is closely linked to the nitrogen dynamics of the site: as soil water nitrate and total inorganic anion concentrations decrease, so too does aluminium (Reynolds *et al., in press*). By doing so, the problems of bromide release to the stream will also be overcome.

4 If possible, vegetation should be introduced which supplies more base cations from the deeper soil and bedrock zones. For example, a stream draining an oak forest near Llyn Brianne is far less acidic than most other streams draining conifer and moorland sites (Bird *et al.*, 1990). Forest management should be viewed in the wider context of maintaining/providing an ecologically healthy environment rather than primarily in terms of timber yield.

5 Use of liming techniques to increase the alkalinity within the soils and streams thereby decreasing the acidity and precipitating environmentally harmful inorganic aluminium. Liming techniques in themselves can adversely affect the natural vegetation: thus minimum coverage of the land by lime is required, both to save costs and protect the natural flora of the area. Pioneering work associated with the Llyn Brianne study has highlighted the value of confining liming to those parts of the catchment which provide the main contribution to storm flow generation in the stream (Jenkins *et al.*, 1991; Waters *et al.*, 1991). Unfortunately these source areas are associated with flora which are particularly sensitive to alkaline and base cation rich environments. The decision to lime is a difficult one whatever strategy is adopted.

6 Minimise the disturbance in and near the stream channel in order to reduce manganese release to the stream.

7 A primary goal — albeit a long-term one — must be to reduce emissions of acidic oxide gases to the environment.

The Plynlimon results show that it is the low flow water quality which deteriorates the most following harvesting. While it is essential that storm flow water quality improves, it is also essential that low flow water quality is maintained above the critical biological thresholds. The application of lime to the hydrological source areas may well be insufficient to improve the situation under these low flow conditions: the flow pathways supplying baseflow are not necessarily the same as those generating stormflow. For example, with the Brianne liming experiment, liming changed the stormflow chemistry but did not always lead to a change in the baseflow chemistry (Jenkins *et al.*, 1991). In order to lime effectively, mathematical models, such as TOPMODEL described earlier, will be required to identify the stormflow source areas and new information will be required to characterise the movement of groundwater.

One of the products of the Plynlimon study has been the identification of the importance of soil and groundwater contributions to the stream. It seems that by passing more water through this groundwater region, better stream water quality will result with lower organic carbon and lower heavy metal concentrations. This promotes weathering processes and increases the alkalinity thereby partially neutralizing the soil water in its passage to the stream. The near-stream bank areas are biologically very active (Fiebig *et al.*, 1990), and they have the potential for removing the nutrient components such as nitrate and bromide which contribute to the water quality problems. Therefore, altering the water flow pathways may provide a means of improving the stream water quality. Set against this, the Plynlimon results suggest that the groundwaters and regions close to the stream bank are particularly sensitive to the anthropogenic changes occurring in the catchments. Consequently, one of the most urgent considerations over the use of remedial treatments is to understand more fully the processes which occur in the near stream bank and groundwater areas. To try to alter flow pathways on a large scale, without a full appreciation of the likely long-term effects, could be very dangerous to the ecology of such delicate ecosystems.

9.3 Water potability

The effect of conifer harvesting has been to increase nitrate and DOC levels: For Plynlimon, the resulting levels remain within the water industry's guidelines. Increased nitrate will not cause water and other environmental problems concerned with algal development in the streams, due to the system being phosphate limited. For dissolved organic carbon, there may be water quality problems due to the presence of colour (visual acceptability) and its reaction with chlorine during water treatment, enhancing the formation of potentially harmful trichloromethane and chloroform (WRc, 1986; Fielding & Horth, 1986; Fawell *et al.*, 1987).

Concerns have already been raised in the water industry over manganese, halogen and aluminium levels in upland waters. Enhanced manganese levels are associated with colour and precipitation in water distribution systems (Chiswell & Mokhtar, 1986; Buckley & Keil, 1990), while questions of toxicity to fish have also been raised (Nix & Ingols, 1981; Reader, 1986). The halogens are important with regard to the chlorination of water for drinking purposes, as potentially harmful trihalomethanes and haloforms are generated (Fielding & Horth, 1986; WRC, 1986).

The present study reveals that manganese values rise, peak and return to control levels within 12 months but for bromide and iodine the pattern of increased levels persists for at least three years. Therefore, there are potentially important additional adverse impacts of deforestation which are not presently considered. Given that the manganese (and possibly DOC) releases occur when soils and alluvium near the stream channel is disturbed, it seems that a more gentle strategy for harvesting these sensitive areas is called for. With regards to aluminium, increases in the stream following deforestation will not only affect the stream biota but it may also constitute problems with drinking water both in terms of discoloration and health risks (Buckley & Keil, 1990) — water treatment processes do not always remove aluminium from solution to acceptably low levels.

Unfortunately, there are no studies, other than the present one, which have monitored these other pollutants and which can set the Plynlimon findings in a regional context. The Plynlimon study does, however, raise a very important 'danger warning'.

10 Conclusion

The deterioration in stream water quality associated with tree harvesting shows three major features. First, the disruption of the natural biological cycles results in increased nitrate and potassium production in the soil water. This flux is transferred from the soil to the stream, quadrupling the concentrations for at least a three-year period: dissolved organic carbon, barium, bromide and iodine typically increase by about 50 per cent. Second, the increased production of nitrate induces an increase of about 50 per cent in the aluminium concentration for the first two years of the felling period. After that, concentrations revert towards the undisturbed levels. Third, the catchment seems either to be acidifying, particularly within the groundwater and lower soil areas, or to have changed its hydrological flow pathways. For example, alkalinity and calcium exhibit marked declines during the summer months following felling.

Given the wide range of components monitored, the results indicate that concerns over deteriorating stream water quality following tree harvesting can be limited to a relatively small range of chemical constituents in stream water: those associated with surface water acidification, dissolved organic carbon, manganese and the halogens.

The observation of a decline in sulphate in the stream, irrespective of whether the trees are harvested or not, may well provide an important example for Wales of the effects of reductions in UK industrial emissions of SO_2. A much longer monitoring programme will be required in order to test for this.

Many of the results presented here fit well with previous observation and speculation over the effects of conifer development and harvesting on UK upland water quality (UKAWRG, 1988, Stevens & Hornung, 1987; Hornung *et al.*, 1989; Adamson & Hornung, 1990). For example, felling of the trees results in a lower interception of mist and gaseous components: this is observed for sodium, chloride and sulphate. Similarly, the removal of trees and the accumulation of brash increases nutrient generation in the soil but limits uptake by the vegetation cover: this is observed for nitrate and potassium.

What was not expected was the decline in the baseflow chemistry. The results show either that the water flow pathways are changing or that our present understanding of the weathering processes is incomplete. The importance of a long-running catchment-based experiment is thus highlighted: a plot or a laboratory study could not assess both the importance of the hydrological pathways and the effect of long- and short-term climatic variability.

Equally, the use of a multi-element approach to studying environmental impacts is vindicated: the results not only focus on which specific chemical components constitute a threat to the ecology of the upland environment: they also provide important fingerprinting techniques for describing complex hydrological, chemical and biological functioning at the catchment scale.

11 Future work: strategic needs

Assessment of environmental impacts on the British uplands is difficult — there is incomplete information on the complex and interactive hydrological, chemical and biological processes operating. A basic need is the maintenance of long-term field studies to monitor the changes in stream water quality following changes in land use and atmospheric pollutant inputs. This need arises for three reasons. First, the rates of build up or depletion of chemicals in the various catchment stores are relatively slow. For example, after three years of felling activity at Plynlimon, sulphate levels in the stream have only declined slightly. Estimation of the rates of sulphate depletion for the soils is important in assessing how quickly improvements in stream water quality will occur. Second, long-term information is required to accommodate the variations associated with yearly fluctuations in climate. At Plynlimon, there have been three dry years over the past seven years of monitoring; these have affected the observed stream water trends. Third, in the case of plantation forestry, the uplands are now subject to felling and replanting. While data on the effects of deforestation are now emerging, the effects of reafforestation remain obscure. On this basis, studies such as those described here are of strategic importance.

Despite the large investment of time and effort over the past decade in the assessment of the impacts of atmospheric deposition and land use change for acidic and acid sensitive systems, major uncertainties remain (Neal *et al.*, 1990a). The present study has led to the identification of six important areas for new research initiatives:

1 The importance of groundwater supplies in generating stream water quality has now been established. These groundwater supply areas should be sampled.

2 Mixing of groundwater and soil waters is important in generating the observed stream water chemistry and water mixing areas should therefore be studied.

3 Despite the known importance of elevated inorganic aluminium concentrations in reducing fish survival, the processes controlling aluminium mobility remain obscure. It will be necessary to investigate these processes.

4 While it is well established that cation exchange and weathering reactions are important in determining soil and hence stream water chemistry, the detailed reactions depicting them need to be described.

5 Knowledge of the input of pollutants to catchments is critical to the assessment of the effects of atmospheric deposition and land use change. Unfortunately, the net input of pollutants cannot be accurately gauged from the data presently collected: it is extremely difficult to separate the materials impacting a catchment from those being cycled through the vegetation. Carefully designed instrumentation will be required.

6 All the predictive hydrochemical models assume that the soil water has a constant chemical composition in each horizon at any given time, but the field studies show large spatial variability. Further work is required to characterise this variability and to integrate it with more representative model formulae.

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Appendix 1 UK studies of the effects of deforestation on water quality

Kershope Forest, Cumbria, England

This study comprised a 'mini-catchment experiment' (drained plots) for 40-year-old Sitka spruce plantations on stagno-humic gleys overlying calcareous till (Adamson & Hornung, 1990). Results show:

1 large increases in nitrate, peaking one year after felling and returning to control levels after four years. Potassium shows a similar pattern of behaviour except that concentrations peaks two years after felling;

2 slight decrease in pH and aluminium in the felled streams compared to the control;

3 sea-salt and sulphate concentrations decline as a result of felling.

Plynlimon, Powys, Wales

Apart from the deforestation studies described in this report, there have been associated studies by the Institute of Terrestrial Ecology (Bangor). In particular, this group monitored the chemistry of a drainage ditch from a clear felled area of the Hore sub-catchment for two years (Reynolds *et al.*, 1992). The work concerned a 40-year-old Sitka spruce stand on stagnopodzol and stagnogley soils. Results show:

1 large increases in nitrate and potassium soon after felling;

2 a slight decrease in pH and aluminium concentration following felling;

3 slow declines in chloride and sulphate concentrations following felling.

Beddgelert forest, Gwynedd, Wales

Here, stream water quality was measured for two small catchments partly clear-felled. The crop was a 50-year-old Sitka spruce stand on stagnopodzol soils (Roberts *et al.*, 1989; Reynolds *et al.*, 1992). Results show:

1 substantial increases in nitrate and potassium with concentrations peaking six to twelve months after felling;

2 a small decrease in pH, but no felling effect for aluminium;

3 a rapid drop in the sea-salt concentrations to about a third of the pre-felling levels after twc years of felling;

4 a small and slow reduction in sulphate concentrations following felling.

Balquhidder and Loch Ard, Scottish Highlands.

Water quality has been determined for forested and moorland areas at both Balquhidder and Loch Ard. A catchment at Balquhidder, comprising 50- to 60-year-old Sitka and Norway spruce on a mixture of acid soils, was 50% clear-felled from 1986 while at Loch Ard, a similar forested area was 65% clear felled in 1988/89. The results of these studies are in the process of being interpreted. Preliminary findings (*personal communication* from Dr Ron Harriman, Freshwater Fisheries Laboratory, Pitlochry) indicate that nitrate and potassium concentrations have greatly increased following harvesting, although there has been little change in pH and aluminium concentration. There has been some decline in sea-salt concentrations.

Appendix 2 Water balance studies at Plynlimon

J.A. HUDSON

The Plynlimon study in perspective

The original aim of the Plynlimon experiment, which forms the backdrop to the hydrochemical study reported here, was to quantify the differences between the water use of the predominantly forest covered Severn catchment, which comprises a large part of the Forestry Commission's Hafren Forest, and the mainly grass covered Upper Wye catchment. The results from the forest were to be compared with those from similar areas of short pasture, to assess the effects on water resources of the predominant land use change in the uplands, from grassland to plantation forest.

At the same time, explanations of the evaporation process in the uplands have been provided by a number of combined water balance and micrometeorological plot scale process studies on the various types of vegetation. Over the years, numerous publications from the study have reinforced the argument that coniferous forestry in wet and windswept upland areas is a recipe for increased water loss from the vegetation, mainly in the form of interception rather than biological transpiration. There are also changes in the catchment response to rainfall that are partly a consequence of the reduced volume of streamflow and partly due to the changes in flow pathways afforded by the initial drainage and ploughing that was carried out to aid tree growth. A summary of the main conclusions from the first twenty years of the study is given in Kirby, Newson & Gilman (1991).

In the early 1980s it became obvious that the impact of mature coniferous forest on stream ecology and water resources, although of prime importance, was not the only facet of upland use that should be considered. Also relevant to the declining quantity and quality of streamflow was the disturbance associated with rapid land use change, for instance initial afforestation, clear felling and grassland improvement. The losses of the nutrients N, P and K, in streamflow was one of the main reasons for deterioration in the quality of some lowland water supplies (Roberts & Marsh, 1987); upland water quality was also threatened by increasing fertiliser applications to grassland (Roberts *et al.*, 1986). It was also implicated as a cause of water quality decline, in certain river reaches, of the major indicator species of environmental quality. Notable among these are the macrophytes, invertebrates and game fish. Although of importance for the ecology of upland rivers, the main fear surrounding the increase in nutrients in upland rivers was the impact on water impoundments and a reduction in the effectiveness of upland water as a dilutant for downstream agricultural, domestic and industrial pollution.

Also of concern was the increasing acidity of upland rivers, caused by the filtering of gaseous, occult and particulate material by the aerodynamically-rough coniferous forest canopy. Physically, the process of pollutant transfer to a forest canopy is very similar to the release of vapour from the canopy, although in the opposite direction. Both processes rely on potential gradients (of pollutant concentration and humidity respectively) and the eddy diffusion caused by advection over the canopy. Thus the quantification of interception and transpiration rates from forest canopies is of relevance not only to water resources but also to the calculation of chemical fluxes through the forest canopy. Interception of a dilute electrolyte and re-evaporation of pure water vapour leads to a concentration of pollutants (SO_2 and NO_x) in the resultant throughfall and stemflow. When coupled with the chemicals in solution reaching the stomata through transpiration, it can be seen that the forest canopy has a very different impact on chemical cycling within catchments than moorland vegetation, particularly when it is kept short by grazing. The corollary is that removal of this vegetation leads to changes in water pathways and geochemical cycling that have a major impact on streamflow chemistry. The disturbance to the soil structure during removal also contributes to the chemical load carried by the streams.

When the Plynlimon experiment was set up in the late 1960s, it was a stated aim that the data collection would proceed through the later part of the forest maturity phase, would encompass the period of felling and would hopefully cover the subsequent regrowth phase as well. By 1985, various vulnerable parts of the Hafren

Forest had suffered from windblow, and it was becoming apparent that the prescribed 50-year-plus forest cycle was not to be realised in many areas. By chance, many of the older trees in the catchment, which were to be found on the steep northerly facing slopes of the Hore subcatchment, had reached the age of economic felling without damage, while younger trees on the more level peaty gley soils had suffered considerable damage. It was not unreasonable therefore to expect that the whole of the lower part of the Hore catchment would be felled imminently and over a short period.

In the spirit of their long-standing support of the research effort at Plynlimon, the Forestry Commission cooperated in a programme of felling in the Lower Hore between 1985 and 1990. Of the 317 ha of the Hore, 139 ha was felled leaving 178 ha of younger trees and grassland in the Upper Hore intact. The Upper Hore was therefore selected as a control against which the effects of the clear felling could be assessed by eliminating the effects of climatic variability. Of the other subcatchments in the Severn, neither the Hafren nor the Tanllwyth were suitable for this purpose because differences had already been noted in their hydrological response and geochemical characteristics. Besides this, they had already both been subjected to a considerable amount of windblow and subsequent clearance. Unfortunately, the tight schedule meant that there was no run-in time with an operational streamflow structure to allow an assessment of the particular hydrological characteristics of the Upper Hore. However its chemistry had been the subject of a restricted study (nutrients and pH) in 1980 and the more rigorous sampling programme begun in 1983 which forms the main thrust of this report.

Framework for the hydrological study

The technique used to estimate the evaporation losses from upland vegetation is the catchment water balance. This method assumes that water loss from the catchment can be calculated in the long term as the difference between precipitation and streamflow, provided there is no deep percolation routed around the streamflow structure. Initially, the two contiguous catchments, the Wye (grassland) and the Severn (67% forested) were instrumented with high quality precipitation and streamflow networks, to ensure the accuracy and precision of a relatively small term (evaporation) calculated as the difference between two larger terms (precipitation and streamflow). Three subcatchments were also instrumented within each of the main catchments. Of these the Hafren, Hore and Tanllwyth in the Severn came under extra scrutiny following the aforementioned decision by the Forestry Commission to clearfell half of the Hore over the period 1985-1990. One of the long-term aims of the experiment was to see whether the quantity of streamflow would recover to grassland levels when tree cover was removed and whether its time distribution and flood response would change.

The hydrological networks within the Plynlimon catchments were designed to include streamflow measurement on the subcatchments, mainly to act as corroborative data for the main catchment comparison, but with a useful subsidiary role in identifying systematic measurement errors in the instrumentation and sampling errors inherent in the networks. To this end, the Hafren, Tanllwyth and Hore were fitted with steep stream flumes, reliable data having since been collected from 1975. Areal rainfall for the catchments is calculated by the Theissen polygon method using data from storage gauges within and just outside each subcatchment. The comprehensive storage gauge network allows calculation of the rainfall to the Upper and Lower Hore areas separately, however no streamflow gauge was fitted to the Upper Hore until 1985, the first year of the felling schedule.

Following the success (after some teething troubles) of the steep stream flumes in providing accurate and continuous flow data (revised calibrations from independent ratings had to be used in some circumstances), the same design was used for the Upper Hore. The dimensions of the Upper Hore flume were chosen to cover a likely range of flows that was interpolated on an areal basis from the long record on the Hore. Construction was started in 1984 and completed in 1985, records starting in the late summer of that year.

Long-term water balance results

The longevity of the Plynlimon catchment experiment has proved invaluable in providing background water balance information to aid the assessment of land use manipulation. Data are available from the main catchments for the periods since 1969 (Wye) and 1972 (Severn), and on the subcatchments since 1973, although reliable data on the latter is from 1975 onwards. Hudson & Gilman (1992) describe the variability of evaporation at Plynlimon in terms of climatic controls, but show that conventional expressions for evaporative demand do not offer a complete explanation of actual variability.

Hudson (1988) emphasised the long standing hypothesis that forests evaporate twice as much water as grassland areas (29% of rainfall from forests compared to 15% from grassland), mainly due to increased interception of rainfall by the forest canopy.

In detail, the results indicate that, over the study period, the annual rainfall has increased marginally, the streamflow has increased at a greater rate and consequently the evaporation from both the grassland Wye and forested Severn catchments has decreased (Tables A1, A2 & A3). Although this marginal increase in rainfall and flow is not significant statistically, a similar pattern of increasing rainfall has been seen elsewhere in Britain (Cole *et al.*, 1991). The evaporation changes, on the other hand, are highly significant. Attempts have been made to explain the decline in terms of biologically driven processes such as damage to the roots of coniferous trees by acid rain (Caspary, 1991). However, it is unlikely that such arguments apply to Plynlimon because here the interception process accounts for most of the loss from forests and is dependent only on foliar density. There is no evidence that foliage densities are declining at Plynlimon — in any case this would not explain the parallel decline in grassland evaporation as shown by the Wye catchment results. The Wye catchment is covered predominantly with vegetation that is well acclimatised to acidic environments (some areas of reseeded pasture are well dosed with lime to discourage acid effects). It seems therefore that the declines are linked with the climate, though it has proved difficult as yet to prove a causal link between observed climate change, evaporative demand and actual evaporation.

The difficulties of performing accurate measurements in hostile climates means that the methods of water balance assessment in upland areas come under extra scrutiny. Precipitation, particularly snowfall, measurement has improved over the years but not to the degree that would cause apparent declines in evaporation. Flow measurement structures in particular rarely perform exactly to design. It is unlikely, however, that the different structures used in the main Wye and Severn experiments would both gradually change in the same sense to give apparent trends in the water balances.

The reduction in evaporation rates must be due to a decline in atmospheric demand for moisture. Declines in radiation input, air temperature and specific humidity deficit have all been identified within the climatic data-set. The declines are particularly noticeable for the main evaporation months, April to September,

Table A1 *Catchment areal rainfall (mm) for the main and subcatchments in the River Severn*

YEAR	SEVERN	HAFREN	HORE	TANLLWYTH	HAFREN+ HORE+ TANLLWYTH
1975	2122		2217	2233	
1976	1731	1732	1785	1745	1755
1977	2720	2712	2838	2735	2767
1978	2452	2442	2555	2560	2503
1979	2797	2841	2841	2851	2842
1980	2635	2641	2692	2763	2677
1981	2776	2775	2826	2938	2816
1982	2338	2335	2333	2461	2349
1983	2650	2563	2765	2751	2669
1984	2135	2102	2178	2147	2138
1985	2355	2319	2424	2451	2378
1986	2720	2739	2792	2790	2767
1987	2354	2360	2435	2306	2385
1988	2637	2682	2734	2592	2693
1989	2410		2445		

Table A2 *Streamflow (mm) for the main and subcatchments in the River Severn*

YEAR	SEVERN	HAFREN	HORE	TANLLWYTH	HAFREN+ HORE+ TANLLWYTH
1975	1454		1549	1619	
1976	1217	1265	1220	1262	1246
1977	2040	2103	2035	2093	2074
1978	1931	1906	1863	1900	1888
1979	2219	2210	2201	2185	2203
1980	2081	2097	2047	2114	2078
1981	2215	2183	2172	2266	2188
1982	1914	2010	1881	2045	1961
1983	2101	2119	2073	2277	2119
1984	1602	1655	1566	1677	1621
1985	1897	1975	1899	2021	1949
1986	2194	2201	2203	2377	2223
1987	1910	1877	1950	2025	1925
1988	2144	2094	2161		
1989	1948	1844	1937		

Table A3 *Annual P–Q (mm) for the main and subcatchments in the River Severn*

YEAR	SEVERN	HAFREN	HORE	TANLLWYTH	HAFREN+ HORE+ TANLLWYTH
1975	668		668	614	
1976	514	467	565	483	509
1977	680	609	803	642	693
1978	521	536	692	660	615
1979	578	631	640	666	639
1980	554	544	645	649	598
1981	561	592	654	672	627
1982	424	325	452	416	388
1983	549	444	692	474	550
1984	533	447	612	470	517
1985	458	344	525	430	429
1986	526	538	589	413	544
1987	444	483	485	281	460
1988	493	588	573		
1989	462		508		

and can be related to the increasingly cloudy conditions that are implied by the higher rainfall now being experienced during the late summer months. However, this does not explain all of the decline in water use in any of the catchments. It is also possible that the decline is partly due to the effects of increasing CO_2 in the atmosphere. Data from Mauna Loa on Hawaii indicates that CO_2 has increased by about 10% over the study period (Houghton *et al.*, 1990) and various workers suggest a strong causal link between declining evapotranspiration rates and CO_2 concentration (Kuchment & Startseva, 1991). Unfortunately, no regular CO_2 measurements have been made at Plynlimon but work is proceeding to link the Plynlimon data with long-term measurements from nearby stations.

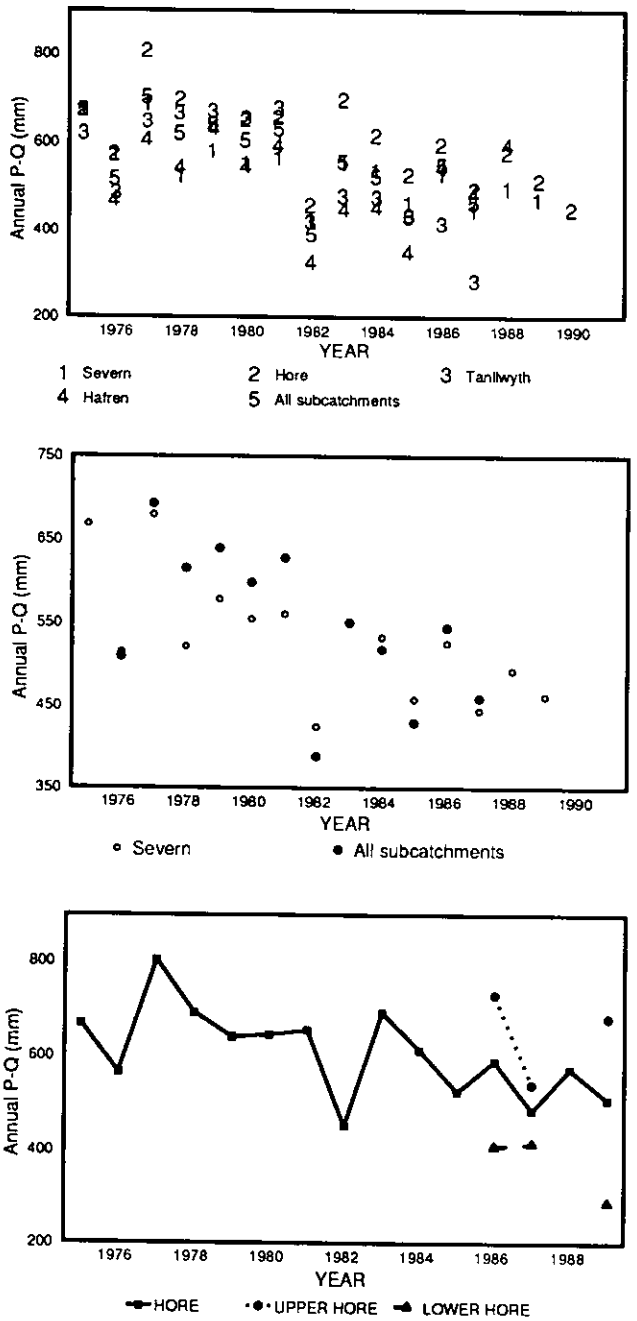

Figure A1 *River Severn, River Wye and Afon Hafren sub catchment water balances (1975–1989)*

Planners of the Plynlimon experiment fortunately had the foresight to provide independent flow measurement assessment for both grassland and forest areas, by instrumenting all the main subcatchments in the Wye and Severn. The period of operation of the subcatchments is not as long as the main catchments. However, in spite of the internal variability of the subcatchment results, for eight of the twelve years' overlap period in the Severn, the agreement between the main catchment and the lumped subcatchments is extremely good (Figure A1). The exception is the evaporation for the period 1978-1981 when the subcatchments are of the order of 75mm higher. This appears to be due to a change in the behaviour of the Tanllwyth relative to the Severn and the rest of the individual subcatchments in 1978, which reverted to normal behaviour in 1982. The reason for this difference remains unclear.

The effects of clearfelling

The most obvious advantage of the experimental/control approach to assessment of land use change effects now becomes apparent because only one subcatchment of the Severn has been subject to the land use change, in this case clear-felling. The interannual variability in precipitation, streamflow and therefore evaporation requires that changes in the Lower Hore can only be discerned with reference to a control, in this case the Upper Hore, a procedure which removes the effect of climatic variation from the analysis. These estimates are not entirely independent as the Lower Hore response is calculated as the areally weighted difference between the whole Hore and the Upper Hore. The results are presented in Table A4 and graphically in Figure A1.

At this juncture, the rainfall input to all three catchments is assumed equal to the Hore, an assumption that is subject to future amendment, but one that does not effect the trend analysis presented here.

Prior to the felling, the differences between the subcatchments are explicable by the altitudinal range of each catchment, the variable proportion of forest within each catchment and minor errors associated with uncertainties in the catchment boundaries. Post-felling there have been slight changes in the relationship between the Lower Hore and the other subcatchments (Figure A1), but the water use has not yet declined to grassland levels. One theory, as yet

Table A4 *The internal water balance of the Hore subcatchment*

YEAR	HORE			UPPER HORE			LOWER HORE		
	P	Q	P-Q	P	Q	P-Q	P	Q	P-Q
1985	2424	1899	525	2424			2424		
1986	2792	2203	589	2792	2062	730	2792	2384	408
1987	2435	1950	485	2435	1895	540	2435	2020	415
1988	2734	2161	573	2734			2734		
1989	2445	1937	508	2445	1766	679	2445	2156	289
1990		2070			2016				

untested, is that the rough brash left on the ground, combined with the regrowth of the previously dormant understorey, allows as high rates of interception as the original tree cover. However, there is a sharp decline in P-Q for 1989 in the Lower Hore relative to the Hore and Upper Hore: further study is required to validate this finding and to provide reliable estimates for subsequent years.

Evaporation loss in the upland UK

Early models of water use were largely based on data from catchment and process studies undertaken at Plynlimon (Calder & Newson, 1979; Bosch & Hewlett, 1982). These models provided the base for the development of rainfall-runoff models. While highlighting the general applicability of many of these models, the continually growing data set also provides a base for identifying their shortcomings. The model that Calder and Newson developed, still holds even though the calibration proved to be based on three abnormal years. However, in detail, the extra data collected since their study shows that evaporation in the uplands is not quite the conservative physical process that it was once thought. In truth, evaporation is influenced by many site specific physical, climatic, chemical and biological factors.

Attempts to extrapolate the results of the Plynlimon experiment to other areas of the UK, using relationships derived between catchment water balances and climatic controls, have been partially successful. However, some UK upland areas (Scotland in particular) experience a more continental climate with a greater proportion of the precipitation falling as snow. This and vegetational differences are important in the water resource context: the vegetational response to snow is different to that of rain; regional differences in vegetation type will influence the impacts of afforestation. The Balquhidder catchments were therefore set up by the Institute of Hydrology to assess such differences. Using techniques developed at Plynlimon, this paired and nested catchment study, with attendant process studies of forest interception under rain and snow conditions, has shown that intermediate height vegetation such as heather, bilberry and grass evaporates more than the short pasture prevalent in mid-Wales (Hall & Harding, 1992) that snow interception by forests can be considerably higher than an equivalent amount of rain (Wright, 1990) and that forest interception itself conforms reasonably well to the hypothesis of Calder and Newson (Johnson, 1990). However, the cold temperatures prevalent in the UK uplands and the associated very short growing season means that further controls on transpiration from grass are introduced (Hall & Harding, 1992). The characteristic layout of forestry schemes in the glens of Scotland (forestry in the valley bottoms and grassland at high altitude) means that the combined evaporation rates of the two vegetation types can be less than the indigenous mixed association of grassland, heather and bilberry.

Future research

The combined results from the Institute's studies within the UK have given, and continue to give, a detailed picture of the evaporation process and the long-term impacts of climate change. However, some aspects of this research require further study. The actual land-use change to forestry, as opposed to the change implied by the paired contemporary catchment study, is being examined at Llanbrynmair Moor

in mid-Wales (Emmett *et al.*, 1991). This study has already indicated that evaporation rates can fall well below potential due to disruption of the vegetation by ploughing. While there are indications that the temperature controls on transpiration that are considerable in Scotland may also have a similar — albeit smaller — effect in mid-Wales, further research is required to substantiate these findings before the results can be incorporated unequivocally into catchment water use models. Similarly at Plynlimon, the spatial variation in the interception process needs to be tackled, both from the point of view of the catchment water balance and from the effects of hydrogeochemical cycling. The relationships between evaporation rates and the climatic, soils and physiological controls need to be better understood before the data can be used to develop models to predict the dominant impacts of climatic change on UK water resource. The UK research in this area has to be put in the context of that undertaken in other parts of the world as the impacts of climatic change are a global problem. This is best achieved by close collaboration in catchment network initiatives such as ENCORE (European Network of Catchments Organised for Research on Ecosystems), ENC (Environmental Change Network) and FRIEND (Flow Regimes from International Experimental and Network Data). However, this type of collaborative research will only be of lasting use if it is underpinned by comprehensive catchment experiments as exemplified by the Plynlimon study: to achieve this, it is vital that secured and adequate funding supports the work.

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Appendix 3 Fluvial sediment studies at Plynlimon

G.J.L. LEEKS

Background

The soil cover of the British uplands is very stable, relative to many other parts of the world. However, if surface vegetation and soils are disrupted, large quantities of weakly-cohesive glacial and fluvio-glacial deposits may be mobilized. Water treatment problems resulting from elevated suspended solids concentrations associated with afforestation of upland water supply catchments have been reported by Austin & Brown (1982) and Stretton (1984). The ground preparation for forestry can loosen surface material, making it easier to mobilise during high rainfall events. Austin and Brown reported the costs of dealing with enhanced suspended sediment outputs following the excavation of forest drainage ditches above Holmestyles Reservoir in the Pennines. A new £78,000 water treatment works was required.

A review of some of the ecological impacts of forestry was carried out by Maitland, Newson & Best (1990). These included elevated fine sediment transport rates and increased deposition of fines in the freshwater habitat (including effects on fisheries and invertebrates). The effects of the ditching/ploughing process on suspended and bed-load sediment yields was studied in Coalburn in the northern Pennines (Robinson, 1980; Robinson & Blyth, 1982).

A larger scale study of these effects has also been carried out in the Cwm catchment, 20km north of Plynlimon (Leeks & Roberts, 1987), and studies of the effects of both clear felling and ditching/ploughing began on the Balquhidder catchments in Scotland in 1986 (Stott *et al.*, 1987; Johnson, 1988). Other British examples of enhanced fine sediment yields associated with afforestation are reported in Burt *et al.* (1984), Francis (1987) and Soutar (1989).

The Plynlimon sediment monitoring network

The monitoring of fluvial sediment yields at Plynlimon began in 1973 with trapping of bedload in the Tanllwyth and Cyff subcatchments. The trap data have indicated consistently higher yields from the forested catchments, three to five times that of the grassland (Painter *et al.*, 1974; Newson, 1980; Leeks & Roberts 1987).

Intensive suspended sediment monitoring in the Plynlimon Experimental catchment began in 1979 as part of a regional study of the fluvial geomorphology of Mid-Wales (Newson & Leeks, 1987). Calculations of yields of both forms of particulate transport showed that although concentrations were relatively low (very rarely exceeding 0.1 gl^{-1}) the suspended sediment outputs were as significant as the bed-load, in terms of the total annual sediment yield.

When the Hore Clear Felling Experiment began, the network of bed-load traps was extended to include minor weirs and traps on some of the drains and feeder streams to Afon Hore. A major trap was also built above the flume at the lower end of the subcatchment. The investigation of the impact of the clear felling of the Hore catchment also led to intensification of the suspended sediment monitoring networks.

Monitoring techniques and flood sampling strategies are described in Leeks (1983). A variety of methods are used: emphasis is placed upon flow-related manual sampling using depth-integrated bulk sampling (USDH-48) and 'gulp' samples taken with bottles. Although no sampling method can be said to produce the 'perfect representative sample', this does avoid many of the problems which have been experienced with the use of automatic samplers: e.g. the small depth range available in channels, which makes it difficult to locate the intake nozzle so as to avoid sampling within the bedload zone.

Manual sampling is supported by continuous turbidity monitoring. The turbidity measurements are of the absorptiometric type. Partech and pHox monitors are calibrated against actual suspended sediment concentrations and Fuller's earth standards. The infra-red and visible light dual-path sensor heads are connected to Squirrel and Campbell Scientific logging systems which integrate turbidity with other water quality parameters at the data logging stage.

Fluvial sediment outputs at Plynlimon

Sediment yields

From 1983 the Hore subcatchment has been extensively instrumented to provide background sediment transport data for two years prior to clearfelling, and to identify post-felling impacts. Before the clear fell, the Hore was yielding lower mean annual bed-load outputs per unit catchment area than the adjacent Tanllwyth forested catchment: 11.8 t km^{-2} compared with 38.4 t km^{-2}. The initial impact of the clearfell was a decline in bedload trapped at the downstream end of the catchment (8.3 t km^{-2} in 1986) due to the build up of sediment behind timber debris within the channel and drains. However, as debris dams broke down or reached capacity, there was a gradual rise in bed-load yield to up to 54.5 t km^{-2} in 1988. Further up the catchment, the effects of timber debris build up were slightly delayed. In one tributary in which the trees were removed earlier than the rest (using skidding techniques) because of windblow problems, the yield increased from 2.16 t km^{-2} in 1983 to 44.28 t km^{-2} in 1984. However, as the felling continued, timber debris built up in the channel, thereby creating a number of debris dams. This led to a fall-off in sediment yield to 9 t km^{-2} in 1985. Under some circumstances, where there is no danger of stream diversion and additional erosion to form a new channel, there may be advantages in delaying or phasing channel clearance work to reduce peaks in enhanced bed-load outputs following felling.

In the case of those subcatchments for which bed-load results are also available, the suspended sediment load yield varied between 24% (Tanllwyth) and 68% (Hore) of total load: the ratios between forest and grassland yields were broadly similar to those for bed-load, i.e. in comparisons with the Cyff, varying between 1.98 and 5.79 times higher yields per unit area in subcatchments with mature forest cover.

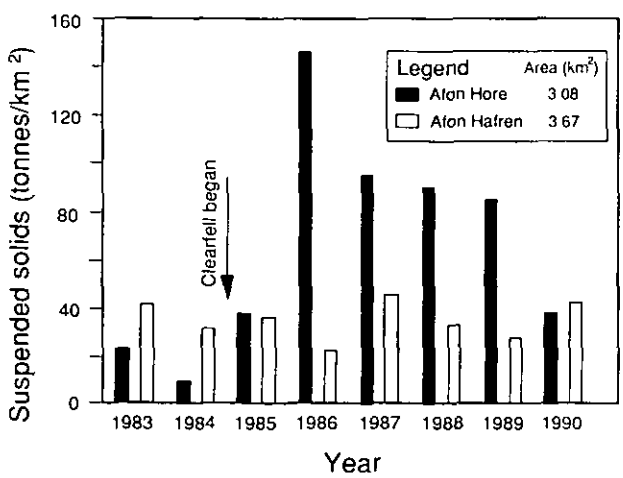

Figure A2 *Annual suspended sediment outputs from the Afon Hafren and the Afon Hore subcatchments*

At the beginning of the felling operation there was an immediate rise in suspended sediment concentrations for any given discharge (Figure A2). This was initially associated with road-widening. Road material was carried direct to the stream network through road drains. Considerable ground disruption by machinery used during the felling work, including forwarders and skidders (in contrast to the dominantly aerial cable techniques used in 1980-81), made large amounts of fines available to the streams. In the first two years following felling, there was an increase in sediment concentrations by an order of magnitude for moderate to high flows. This increase was reflected in higher annual yields of suspended sediment from 24.4 t km^{-2} rising to 141.0 t km^{-2} in 1986.

A further change in the variations in suspended load has been the occurrence of short-lived pulses of high suspended load during low or moderate flows which are unrelated to natural entrainment processes. These are associated with a variety of activities such as the movement of heavy machinery through the channel/ditch system, drain/culvert clearance and road modifications. The combination of low flows with high suspended solids can lead to within-channel deposition of fines above normal gravel and cobbles of the stream bed. This may have a deleterious effect upon channel habitat. Concentrations of up to 0.380 gl^{-1} have been measured in Mid-Wales streams as a result of the movement of heavy machines across stream beds.

Sources of sediment in forested streams

In upland streams, sediment is derived from the catchment surface, erosion of the channel banks and from within-channel stores. In forested catchments, as in some improved agricultural catchments, there may also be additions from tracks, plough furrows and drains. The main sediment source of the higher bed-load yields in the Hore are the network of drainage ditches within the catchment. Many of these drains lead directly into natural watercourses (this is not the case in present day afforestation schemes). The excavation of ditches through the protective cover of vegetation and peat exposes the subsoil to erosion.

Newson (1980) carried out field measurements to compare gradients and flow velocities in open ditches. The surveys revealed that ditches in blanket peat and gleyed soil were stable at gradients up to 15°. However, where the colluvium below the peat or gley was penetrated, significant erosion was apparent. Critical

velocities for erosion and transport of the colluvial material ranged from 0.36 to 2 ms^{-1}. This work suggested that in sensitive materials ditch gradients should be very gentle, i.e. 2° or less.

Joint work with Liverpool University and the UK Atomic Energy Authority (Harwell) has clarified the likely sources of suspended sediment in Plynlimon streams. Arkell (1985) analysed filtered bulk samples of suspended sediment from a downstream location on the Severn (Abermule). These were compared with measurements of magnetic parameters from *in situ* sediments within the Plynlimon experimental catchments and alluvial reaches of the River Severn to indicate sources, including forested areas, stream channel and banks.

The use of magnetic analysis in the experimental catchments has been extended in combination with radiometric techniques following the nuclear accident at Chernobyl in April 1986 (Bonnett, Leeks & Cambray, 1989). The strong fixation of caesium-137 to clay minerals provided an opportunity to study sediment transport through the upland system. Chernobyl-derived debris was deposited on Plynlimon in early May 1986. An extensive network of soil-coring sites was established.

Comparisons between the expected distribution of deposition and measured Chernobyl fallout activity in the soil cores indicated zones of soil erosion and deposition in the two years following May 1986. Decline in the expected ^{137}Cs inventory of more than 20% was interpreted as evidence of erosion of fine topsoil. Erosion was apparent in the upper Hore and particularly the lower half of the Hore, Tanllwyth and Cyff catchments. Soil cores from lower parts of the Iago and Gwy down to the Cyff confluence had values of more than expected activity, indicating deposition. Hence there is evidence of post-Chernobyl redistribution of topsoil, although some of the losses may have been caused by vertical and lateral migration of radio-caesium from surface peats in the highest parts of the catchments.

There is also evidence of removal of caesium from the catchments attached to the fluvial sediments. Samples from both bedload traps and specially designed suspended-load settling tanks have a high Chernobyl content relative to total caesium activity — 60 per cent in suspended load and 32 per cent in bedload. This is an indication of the relative importance of top-soil as a source for the different types of transport. The high Chernobyl component in suspended sediment points to a top soil source while the lower activity levels in bed-load suggests a sub-soil source of sediment supply, for instance the drains. This is backed up by magnetic analyses which point to channel and sub-surface sources for bed-load and surface sources for suspended load. In total, the suspended-load outputs accounted for 95.5 to 98 per cent of the fluvial outputs of Chernobyl caesium. Comparisons between caesium yields in fluvial sediments with the total Chernobyl derived caesium indicated that in 1988 and 1989 approximately 0.08 per cent per annum was removed from the catchment in fluvial outputs. Bonnett *et al.* (1989) also provide evidence of supply limitations in the fluvial entrainment of Chernobyl-tagged sediments. Bedload trapped in the River Severn catchment between November 1987 and January 1988 did not contain Chernobyl material, indicating temporary exhaustion.

Changes in the caesium budgets have also taken place as a result of felling practices. Preliminary evidence reported by Bonnet & Leeks (1989) indicates that there has been an enrichment in Chernobyl-derived caesium in the lower Hore catchment in comparison with other parts of the catchments. Bonnet & Leeks point out that little attention has been paid to the attachment of radio-caesium to the bed-load. Although much of the coarse bed-load is relatively inert, some, more chemically-active, fines are attached to it. This represents a secondary routeway for the downstream transfer of chemical substances which is subject to slower, more erratic mobilisation. The data also suggests that forest harvesting and mechanical site preparation may result in an increased supply of ^{137}Cs and ^{134}Cs to the bed-load part of the sediment outputs from the upper Severn.

Storage of sediment

In most studies of the afforestation stage, a high output of fines has been noted over the first few high flows. This is associated with open plough furrows which run downslope, unlike the contour ploughing practice in the lower parts of the main Cwm catchment. Francis (1987) and Francis & Taylor (1989) reported significant enhancement in sediment yields from upper parts of a tributary subcatchment of the Cwm where downslope ploughing was practised. This enhancement in sediment loads was not translated downstream to the main Cwm catchment, for example in flood samples of suspended sediment taken at the Cwm flow gauging station. The reason for this appears to be that below the study catchment used by Francis, the tributary stream disappears into a large, low gradient, boggy area within which there are several large depositional delta forms. This appears to be a 'sink zone' in which the enhanced sediment outputs from the forest were

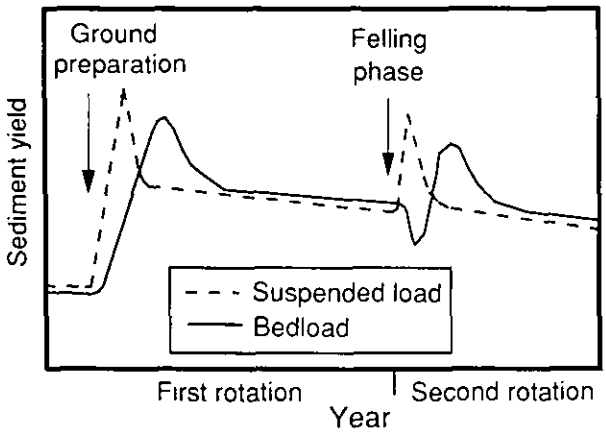

Figure A3 *Summary diagram of fluvial sediment yields from upland catchments given conventional forest practice for both bedload and suspended particulate loads over the forest rotation*

redeposited. This example indicates the caution necessary in the use of headwater results as a means of predicting downstream effects.

Sediment yields over the forest rotation

The sediment yields at each stage of the forest rotation, given conventional forestry practice in Mid-Wales, is as follows (Figure A3):

a *Afforestation Stage* - most British studies have indicated a rapid rise in fine sediment outputs: significant increases in bed-load responses occurred because of track-building, for example.

b *Mature Forest Stage* - a long term enhancement in sediment output over several decades has been identified in drained mature forested catchments, amounting to three to five times as much as nearby grassland catchments.

c *Felling Stage* - at the end of the forest rotation, further increases in sediment yield above those of mature forestry occurs. Track modifications led to an immediate rise in suspended load concentrations by an order of magnitude in the Hore, while bed-load response was initially a fall in yield, due to formation of debris-dams in the upper reaches and drains. This was followed by an increase in yields to five times that of pre-felling.

Reducing particulate transport in forests

The Plynlimon results have formed a significant part of a body of evidence concerning the impacts of forestry upon British upland streams. It should be noted that the enhanced sediment yields are lower than in many studies reported elsewhere in the world and the data does not relate to the best forest practice now available or put forward in the new Forestry Commission Guidelines. In addition, slight changes in forest practice can markedly reduce sediment problems. Some of these ameliorative measures, based upon British case studies and observed good practice by foresters, are listed below:

a when excavating ditches, gradients of less than 2° are required to prevent scour (Newson, 1980);

b new forest drains and plough furrows should be stopped short of the streams;

c the most appropriate time to plough is spring and early summer as some revegetation is possible, thereby reducing the likely suspended sediment outputs over the following year (Burt *et al.*, 1984);

d drains which have suffered erosion in the first rotation could be modified for the second rotation by blocking off outlets to streams or dispersal of flow along new cross-drains;

e following felling, it is often considered desirable to clear drains of debris. However, this can result in loosening of material in drains, leading to high suspended sediment concentrations at moderately low flows, leading in turn to deposition of significant quantities of fine sediment over river gravels. This is highly undesirable at certain times of the year because of its effects upon bed biota. In cases where there is no major blockage of the channels, phasing of this operation may be advantageous. This will also reduce the coarse sediment peak as material held up temporarily behind small debris dams;

f movement of machinery through stream channels should be minimised;

g the road drains and loose road embankment materials should be isolated from the streams. Gully development in embankments close to streams should be stopped, eg. by plastic netting or similar stabilising materials.

One of the most important aspects of the Plynlimon sediment results is the long-term record of enhanced sediment yields associated with open drains. The implication for forest management is that where such erosion is perceived as a particulate pollution problem it is better to intervene to reduce sediment outputs

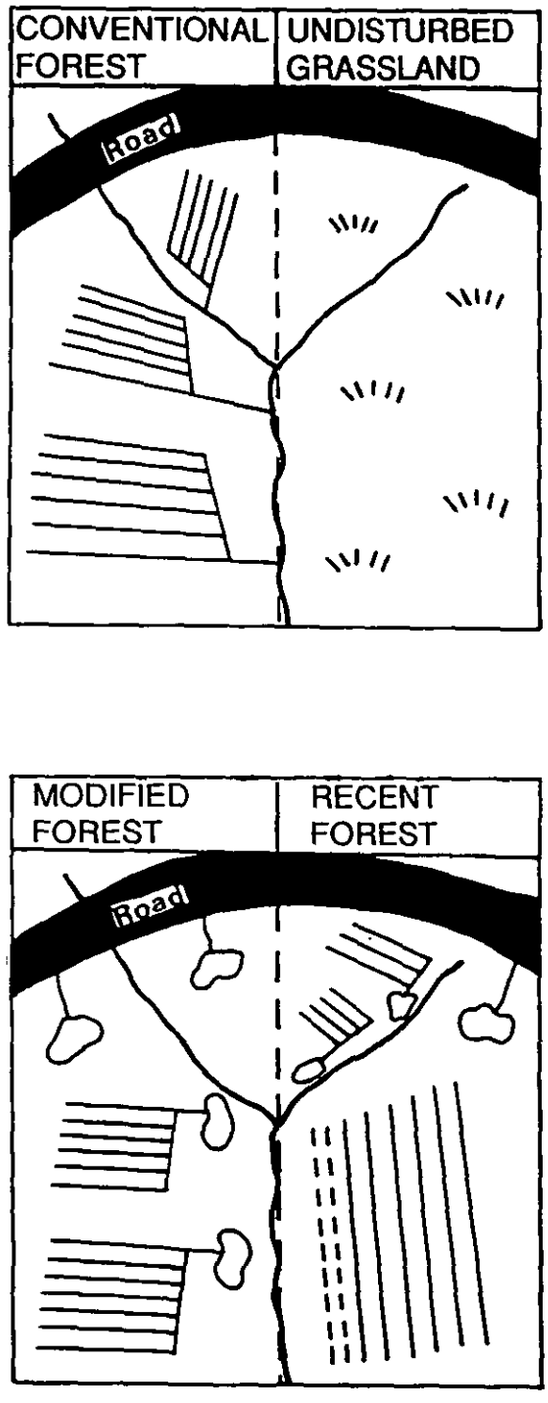

Figure A4 *Generalised plans of upland catchment land use, showing differing degrees of isolation of catchment sediment sources from stream channels*

than to assume that erosion rates will diminish with time (as often occurs with natural erosion inputs). The beginning of the second rotation provides a good opportunity to get heavy plant into the felled forest areas to modify old, badly-eroding drain and road systems. Figure A4 summarises some of the means of reducing sediment outputs both in new plantations and in older ones.

Future research

A number of follow-up studies could yield valuable additional information about the movement of particulate materials through forested streams. Some of these which would be relevant to upland river management are:

1 investigation of new approaches to ground preparation, e.g. ripping techniques;

2 further study to provide additional scientific support to ameliorative techniques, e.g. buffer strips, drain modifications or traps. For example, although buffer strips will reduce sediment inputs to streams, our understanding of the processes, and of the most effective geometries under differing hydrological inputs, topographies, soils and forest practice, is poor;

3 research on the impacts of afforestation or felling in blocks upon nearby watercourses;

4 investigation of the impacts of phasing forestry operations upon stream water quality and habitat;

5 study of the chemical interaction between the solutional and particulate sources, stores and transported loads within forested areas, especially at times of high sediment mobilisation;

6 development of rapid survey techniques to detect and assess any short- or long-term sediment pollution impacts.

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